REDUCTION OF MOLYBDENUM AND TUNGSTEN HEXAFLUORIDES TO THE PENTAVALENT STATE.

A thesis submitted to the University of Glasgow for the degree of M.Sc. in the Faculty of Science.

by

NASHUNMENGHE BAO

Department of Chemistry,

University of Glasgow.

November 1989.

I would like to dedicate this

work to my parents.

ACKNOWLEDGEMENTS.

I would like to express my thanks and deep respect to my supervisors, Dr. J.M. Winfield and Professor D.W.A. Sharp for their help, guidance and encouragement throughout this work.

My thanks are also due to all my fellow research colleagues, Mr. L. McGhee, Dr. J. Thomson, Dr. R.M. Siddique and others for their help and assistance. My thanks also go to Mrs. Liz Hughes for typing this thesis and the technical staff members of the Infrared Laboratory, and Glass Blowing Workshop for their help and cooperation.

I would like to thank the Ministry of Agriculture, People's Republic of China for the scholarship awarded to me and Glasgow University for a common bursary.

My wife deserves a special mention for her love and encouragement.

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Reaction of Ionic Iodides with Molybdenum and Tungsten Hexafluorides.

SUMMARY

This thesis presents a study of the behaviour of higher oxidation state fluorides of molybdenum and tungsten towards some reducing agents, ionic iodides or Mo and W metals, in three different solvents SO_2, MeCN and CH_2Cl_2.

Chapter One summarises previous studies made of higher oxidation state transition metal fluorides, particularly those of molybdenum and tungsten. It is concerned with the preparations, structures and redox chemical behaviour under different conditions and in different solvents.

Chapter Two describes the experimental techniques, for example vibrational spectroscopy or cyclic voltammetry etc., which were used to complete the present work.

In Chapter Three, the redox behaviour of MF_6 and MF_6^- salts (M = Mo, W) towards ionic iodides in CH_2Cl_2 and SO_2 is reported. The reactions between iodides and MF_6 are quite straightforward in SO_2. The products are identified as MF_6^- salts on the basis of their infrared spectra. However, in CH_2Cl_2, although Bu_4NI is soluble and reduces MF_6 readily to MF_6^-, the alkali metal iodides, NaI and KI are insoluble; as a result these reactions are slow and incomplete. The iodide Bu_4NI cannot reduce MF_6^- to MF_6^{2-} in these solvents, although a mixture of MoF_6^- and MoF_6^{2-} salts is obtained from the reaction of an equi-molar mixture of $NaMoF_6$ and NaI in SO_2 at -60^oC. The reaction of $[Cu(MeCN)_4][MF_6]$ and Bu_4NI in CH_2Cl_2 leads to the formation of Bu_4NMoF_6 and CuI. The products described in this chapter have been identified by their

infrared and electronic spectra. The magnetic moments obtained over the temperature range from 80 K to 298 K for some MoF_6^- salts are discussed.

In Chapter Four, the electrochemical properties of some hexafluoromolybdates and ionic iodides in the three solvents MeCN, CH_2Cl_2 and SO_2 are described and discussed. The redox couples MoF_6/MoF_6^- and MoF_6^-/MoF_6^{2-} are compared with the couples arising from the iodide anion by means of cyclic voltammetry. The half-wave potentials of these couples indicate that the iodide, Bu_4NI can easily reduce MoF_6 and WF_6 to the MoF_6^- and WF_6^- anions respectively, but the iodide has no capability of reducing MF_6^- salts to MF_6^{2-} salts (M = Mo, W) in MeCN and CH_2Cl_2.

Chapter Five deals with a study of the reduction of MF_6 by M metal (M = Mo, W) in MeCN. Consistent with previous work, MoF_6 is reduced by Mo powder at 150°C to give $(MoF_5)_4$, and $(MoF_5)_4$ reacts with MeCN to produce the complex MoF_5.NCMe. A new improved preparation of this complex MoF_5.NCMe is reported. Molybdenum hexafluoride is reduced by molybdenum metal in MeCN at room temperature to give MoF_5.NCMe. A similar reaction occurs between WF_6 and tungsten metal in MeCN at room temperature to produce WF_5.NCMe. These complexes have been characterized by infrared spectroscopy and microanalysis. The hexafluorides, MoF_6 and WF_6 are also reduced by W and Mo metals respectively in MeCN at room temperature, although definitive characterization of the products has not been achieved.

Anhydrous copper(II) fluoride, CuF_2, reacts slowly with

MoF_5.NCMe at room temperature in MeCN. The product is a soluble Cu^{2+} salt. The complex MoF_5.NCMe also reacts with Bu_4NI to release small amounts of I_2.

CHAPTER ONE

INTRODUCTION.

Transition metal fluorine chemistry has been a subject of great interest to many chemists for many years. Much work in inorganic chemistry is carried out in solution, therefore, solution chemistry attracts the interest of many workers. The majority of inorganic reactions have been investigated in aqueous solution and the properties of a large number of elements and compounds have been well characterized. Some metal cations have unstable oxidation states in aqueous solution because of hydrolysis or disproportionation, for example, the Cu(I) ion is not stable in aqueous solution because it undergoes the disproportionation reaction to give Cu(II) and Cu (equation 1-1).

$$2Cu^{+} \longrightarrow Cu^{2+} + Cu^{o} \qquad (1\text{-}1)$$

However Cu(I) can exist in contact with water as insoluble solids, such as CuCl, CuBr and CuI, or it exists in soluble complexes with suitable ligands, for example in $[Cu(CN)_4]^{3-}$, [1] $[Cu(py)_4]^{+}$, [2] $[CuCl_3]^{2-}$, [3] and $[Cu(NH_3)_3]^{+}$. [4] Unstable oxidation states of cations also can be stabilized by using a suitable solvent. Therefore, anhydrous solvents can be used to stabilize cations which have unstable oxidation states in water. For instance, Cu metal can be oxidized by MoF_6 or WF_6 to form the stable complexes $[Cu(MeCN)_4][MoF_6]$ or $[Cu(MeCN)_4][WF_6]$ respectively in MeCN. [5]

Transition metal chemistry is concerned with the coordination of ligands to a metal centre. The formation of coordinated compounds is based on the formal concept of electron pair donation from ligands to the central metal cation. Thus complex formation is basically an interaction between a Lewis acid and a Lewis base. Hard acid cations prefer to interact with hard base solutions while soft acid cations prefer to interact with soft bases. For example, phosphines

(R_3P) and thioethers (R_2S) have a much greater tendency to coordinate with Hg^{2+}, Pd^{2+} and Pt^{2+}, but ammonia, amines (R_3N), water and fluoride ions prefer Be^{2+}, Ti^{4+} and Co^{3+}.[6]

During more than one hundred years, transition metal fluorine chemistry has been developing steadily, and now it is a mature scientific research area.

1-1 Transition Metal Fluorides.[7]

The number of transition metal fluoride compounds characterized is enormous, but the best known d-block binary transition metal fluorides are collected in Table (1-1). The physical properties of the transition metal fluorides vary regularly when oxidation states change. In general, the volatilities of the fluorides of an element increase when the oxidation state of the element increases. Many hexafluorides are very reactive and corrosive substances and normally must be handled in Ni or Monel apparatus. The hexafluorides decrease in stability with respect to dissociation into F_2 and lower fluorides in the order WF_6 > ReF_6 > OsF_6 > IrF_6 > PtF_6, and RuF_6 > RhF_6, and the volatility of the compounds also decreases with increasing mass.

Some pentafluorides can be obtained by controlled fluorination of the metal. The pentafluorides are also very reactive and hygroscopic substances. The tetrafluorides may be obtained by the one electron reduction of the respective pentafluorides using suitable reducing agents.

Molybdenum and tungsten, which are the elements used in the present work, are members of the 4d and 5d series respectively. Molybdenum has four binary fluorides, the hexafluoride, pentafluoride, tetrafluoride and trifluoride, while tungsten has two

Table 1-1 The Best Known d-block Binary Transiton Metal Fluorides.

Compounds / Oxidation states of metal / Metal elements	1	2	3	4	5	6	7
Sc			ScF_3				
Ti			TiF_3	TiF_4			
V		VF_2	VF_3	VF_4	VF_5		
Cr		CrF_2	CrF_3	CrF_4	CrF_5	CrF_6	
Mn		MnF_2	MnF_3	MnF_4			
Fe		FeF_2	FeF_3				
Co		CoF_2	CoF_3				
Ni		NiF_2					
Cu		CuF_2					
Y			YF_3				
La			LaF_3				
Zr		ZrF_2	ZrF_3	ZrF_4			
Hf				HfF_4			
Nb				NbF_4	NbF_5		
Ta					TaF_5		
Mo			MoF_3	MoF_4	MoF_5	MoF_6	
W				WF_4	WF_5	WF_6	
Tc					TcF_5	TcF_6	
Re				ReF_4	ReF_5	ReF_6	ReF_7
Ru			RuF_3	RuF_4	RuF_5	RuF_6	
Os				OsF_4	OsF_5	OsF_6	
Rh			RhF_3	RhF_4	RhF_5	RhF_6	
Ir			IrF_3	IrF_4	IrF_5	IrF_6	
Pd		PdF_2		PdF_4			
Pt				PtF_4	PtF_5	PtF_6	
Ag	AgF	AgF_2	AgF_3				
Au			AuF_3		AuF_5		

well characterized binary fluorides, tungsten hexafluoride and tungsten pentafluoride.[7,8] Molybdenum and tungsten hexafluorides are volatile, colourless liquids at room temperature and are very hygroscopic. Molybdenum hexafluoride is the stronger oxidizing agent. The yellow-green, non-volatile solid MoF_4 can be prepared by the one electron reduction of MoF_5 using silicon as the reducing agent in anhydrous HF.[9] Yellow-green non-volatile MoF_3 is obtained by reaction of Mo with MoF_6 at 400°C.[7]

The boiling points of MoF_6 and WF_6 are 35.0°C and 17.0°C respectively. Therefore these fluorides can be handled in vacuum system easily and can be purified by vacuum distillation. The pentafluorides are much less volatile than the hexafluorides, the boiling point of molybdenum pentafluoride is 213°C.

Tungsten pentafluoride undergoes disproportionation reaction to WF_6 and WF_4 at temperatures above 25°C,[7] and this may be the reason that the boiling point of tungsten pentafluoride is not known.

1-2 The Preparation of Molybdenum and Tungsten Hexafluorides and Pentafluorides.

1-2-1 Preparation of Molybdenum and Tungsten Hexafluorides.

Several methods are available for the preparation of molybdenum hexafluoride and tungsten hexafluoride. Among these, the direct fluorination of the metal with elemental fluorine at 300-350°C is the most satisfactory and the easiest one to use. Activated NaF which absorbs HF, enables Pyrex glass apparatus to be used to collect the product.[10] Other fluorinating agents,[11] such as chlorine trifluoride and bromine trifluoride can be used also for the preparation of molybdenum and tungsten hexafluorides

from the metals. The main disadvantage of using bromine trifluoride in the preparation is that the hexafluoride has to be separated from elementary bromine which is miscible with the hexafluoride.

Both molybdenum and tungsten dibromides react with anhydrous hydrogen fluoride at temperatures greater than 550°C to give the metal hexafluorides.[12,13] The reactions are believed to proceed through the initial formation of the metal difluoride followed by disproportionation to the metal and the metal hexafluoride (equations 1-2 and 1-3)

$$2MoBr_2 + 4HF \rightleftharpoons 2MoF_2 + 4HBr$$

$$3MoF_2 \xrightleftharpoons{800^{\circ}C} 2Mo + MoF_6 \qquad (1\text{-}2)$$

$$2WBr_2 + 4HF \rightleftharpoons 2WF_2 + 4HBr$$

$$3WF_2 \xrightarrow{600^{\circ}C} 2W + WF_6 \qquad (1\text{-}3)$$

Other preparations of molybdenum hexafluoride include the fluorination of the hexavalent oxide with bromine trifluoride, sulphur tetrafluoride or hydrogen fluoride.[14] Halogen exchange reactions also can be used to prepare WF_6. Reagents include fluorinating agents such as hydrogen fluoride, arsenic trifluoride and antimony pentafluoride (equations 1-4, 1-5 and 1-6).[11]

$$6HF + WCl_6 \longrightarrow WF_6 + 6HCl \qquad (1\text{-}4)$$

$$2AsF_3 + WCl_6 \longrightarrow WF_6 + 2AsCl_3 \qquad (1\text{-}5)$$

$$3SbF_5 + WCl_6 \longrightarrow WF_6 + 3SbF_3Cl_2 \qquad (1\text{-}6)$$

1-2-2 Preparation of Molybdenum Pentafluoride and Tungsten Pentafluoride.

Molybdenum pentafluoride was first isolated from the reaction between elementary fluorine and molybdenum carbonyl at low temperature.[15] Molybdenum carbonyl treated with fluorine diluted in nitrogen at -75°C gives an olive-green product of composition Mo_2F_9. The nature of this substance is still not clear. When the temperature is raised to 150°C it yields non-volatile MoF_4 and volatile yellow MoF_5.

Molybdenum hexafluoride can be reduced by molybdenum hexacarbonyl to give MoF_5 (equation 1-7)[7,16]

$$5MoF_6 + Mo(CO)_6 \xrightarrow{25^\circ C} 6MoF_5 + 6CO \qquad (1\text{-}7)$$

Molybdenum pentafluoride can also be obtained by the reduction of MoF_6 with molybdenum metal at 150°C (equation 1-8),[17]

$$Mo + 5MoF_6 \longrightarrow 6MoF_5 \qquad (1\text{-}8)$$

When molybdenum metal powder is treated with elemental fluorine, diluted with oxygen-free nitrogen, the products include MoF_5 (equation 1-9).[18]

$$2Mo + 5F_2(\text{dilute}) \xrightarrow{400^\circ C} 2MoF_5 \qquad (1\text{-}9)$$

However, MoF_5 is contaminated with a large proportion of the oxytetrafluoride from which complete separation is very difficult. It has been reported that the interaction of molybdenum hexafluoride with phosphorus trifluoride produces molybdenum pentafluoride and phosphorus pentafluoride, there was no evidence of the formation of any molybdenum fluoride lower than MoF_5 (equation 1-10),[19]

$$2MoF_6 + PF_3 \longrightarrow 2MoF_5 + PF_5 \qquad (1\text{-}10)$$

A more recently developed method for the preparation of MoF_5 is the one electron reduction of MoF_6 with silicon powder or hydrogen gas in anhydrous HF.[9]

$$2MoF_6 + H_2 \xrightarrow[3\ days]{HF} 2MoF_5 + 2HF \qquad (1\text{-}11)$$

$$4MoF_6 + Si \xrightarrow[1\ hr]{HF} 4MoF_5 + SiF_4 \qquad (1\text{-}12)$$

Tungsten pentafluoride is obtained by quenching the product of the reaction of W with WF_6 at high temperature (530 - 730°C).[7] The solid is unstable, with respect to the disproportionation reaction giving WF_4 and WF_6 at about 50°C.

Little is known about tetrafluorides, this may be due to the unsatisfactory nature of the synthetic methods used for their preparation.

1-3 Structure and Bonding of the Hexafluorides.

1-3-1 The Structure.

There has been a great deal of interest in binary transition metal fluorides from the structural point of view. The transition metal hexafluorides have octahedral arrangements of six fluorine atoms around the central metal atom. In the solid state, the hexafluorides undergo a phase transition from a low temperature orthohombic form to a high temperature cubic form at -8.7°C for MoF_6 and -8.2°C for WF_6.[20] T.H. Levy et al studied the crystal structures of the hexafluorides, MoF_6, WF_6 and UF_6 at -196°C by powder neutron diffraction.[21] The metal-fluorine bond lengths do not change significantly on cooling to -196°C, but the octahedra pack more efficiently, and the structure of the solid more closely approaches the ideal hexagonal close-packing arrangement of the fluorine atoms.

It has been determined that the M-F distance in MoF_6 (1.820 Å) is smaller than that for WF_6 [22] (1.832 Å). Furthermore, the molecular volumes of MoF_6 in the orthorhombic (106.6 $Å^3$) and cubic (120.9 $Å^3$) phase of the solid are significantly smaller than those of WF_6 (108.5 A^{o3} for orthorhombic, 123.8 $Å^3$ for cubic). However these Mo-F and W-F bonds are much shorter than that of U-F bond (2.00 Å).[21] Therefore the MoF_6 and WF_6 molecules have a more spherical shape than the UF_6 molecule. Molecular vibrations are greater in MoF_6 and WF_6 than in UF_6, since their molecules have less tendency to interlock. In the vapour phase, the hexafluorides also have octahedral symmetry.[20]

1-3-2 The Bonding

A Raman spectroscopic study carried out on hexafluoride vapours showed that the values of ν_1 for the 4d and 5d transition metal hexafluorides decrease with increase in atomic number in a transition series.[20] The ν_1 mode is the completely symmetrical vibration and may be taken as the frequency closest to a measure of the bond strength, because the vibration does not change the symmetry of the molecule and it does not involve any movement of the heavy central metal atom. From the dramatic change of the ν_1 mode, it can be inferred that the bond strength decreases. This sequence is consistent with the decrease in the stability of the hexafluorides within a row from left to right (see Section 1-1). These trends can be understood if it is assumed that some π-bonding is occurring in the hexafluorides by donation of fluorine electrons into the vacant t_{2g} orbitals of the metals, in addition to σ bonding. As the number of electrons in the metal t_{2g} orbitals increases across the series, the π-bonding effects decrease, resulting in decreasing

stability. Therefore, π-bonding should decrease from WF_6 to PtF_6 according to this assumption. In PtF_6, the σ bond electrons will be very strongly polarized towards the Pt atom because of the smaller π-bonding in PtF_6 and greater atomic number of Pt. As a result, the electron density on the outside of the F ligands decreases. These would explain the greater tendency of the F ligands in PtF_6 to lose metal-F bonding ($PtF_6 \longrightarrow PtF_5 + F^{\cdot}$) electrons causing dissociation:

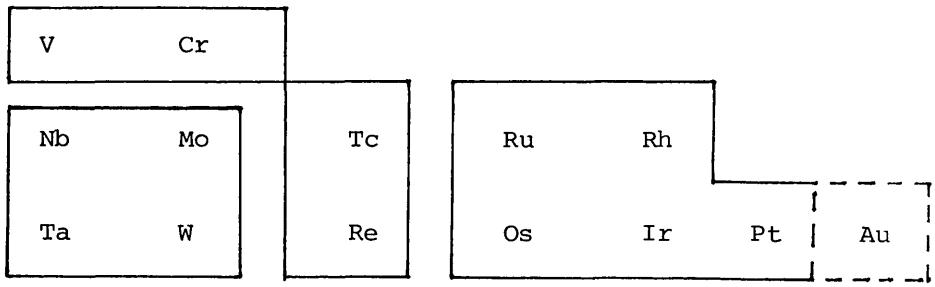
$$PtF_6 \longrightarrow PtF_{(6-x)} + X/2\ F_2 \qquad (1\text{-}13)$$

1-4 Structure of Pentafluorides.

The pentafluorides of all the 4d and 5d elements from Nb and Ta to Pt are known with the exception of palladium pentafluoride.

The structures of d-block pentafluorides change from cubic close packing to hexagonal close packing of fluorine atoms from left to right across the block.[20,23] Three types of structures, illustrated by niobium, vanadium, and rhodium pentafluorides, have been reported.[23] The three groups are indicated in Table 1-2.

Table 1-2 The three structural types of transition metal pentafluorides.



Pentafluorides of tantalum, molybdenum and tungsten have the niobium

pentafluoride structure, those of chromium, rhenium and technetium have the vanadium pentafluoride structure, and rhodium, ruthenium, osmium, iridium, platinum and (possibly) gold pentafluorides are isostructural.

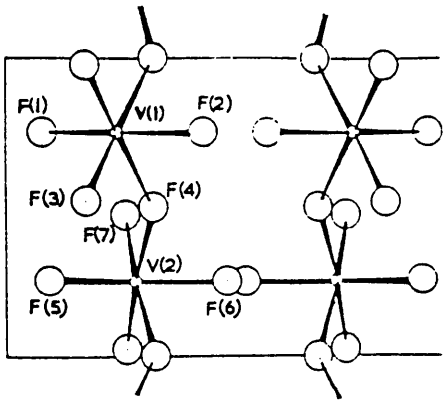
In the three structural types, the coordination of the metal atoms is the same, with a distorted octahedral arrangement of fluorine atoms. Two cis-fluorine atoms in the octahedron form bridges to two other metal atoms, and there are four terminal fluorine atoms. In the vanadium pentafluoride case, the octahedral units form an infinite zig-zag chain with the V-F-V angle at 150°C. The other two structural types are tetramers distinguished by the angles at the bridging fluorine atoms. For niobium pentafluoride, the Nb-F-Nb angle is close to 180° giving linear bridges and a square arrangement of metal atoms. For rhodium pentafluoride, the Rh-F-Rh angle is close to 135° giving angular bridges and a rhombus of metal atoms (Figure 1-1).

1-5 Comparisons of the Chemical Reactivity of Some Transition Metal Higher Oxidation State Fluorides.

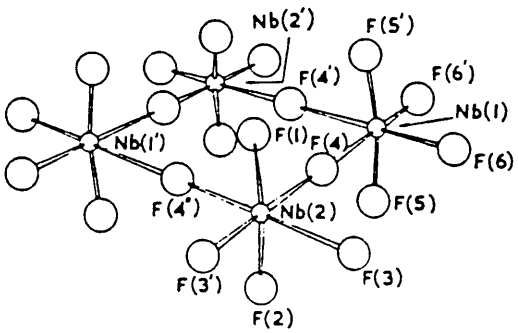
In general, the chemical reactivities of transition metal fluorides increase markedly as the oxidation state of the metal increases.[24]

1-5-1 Electron Affinities of MoF_6 and WF_6

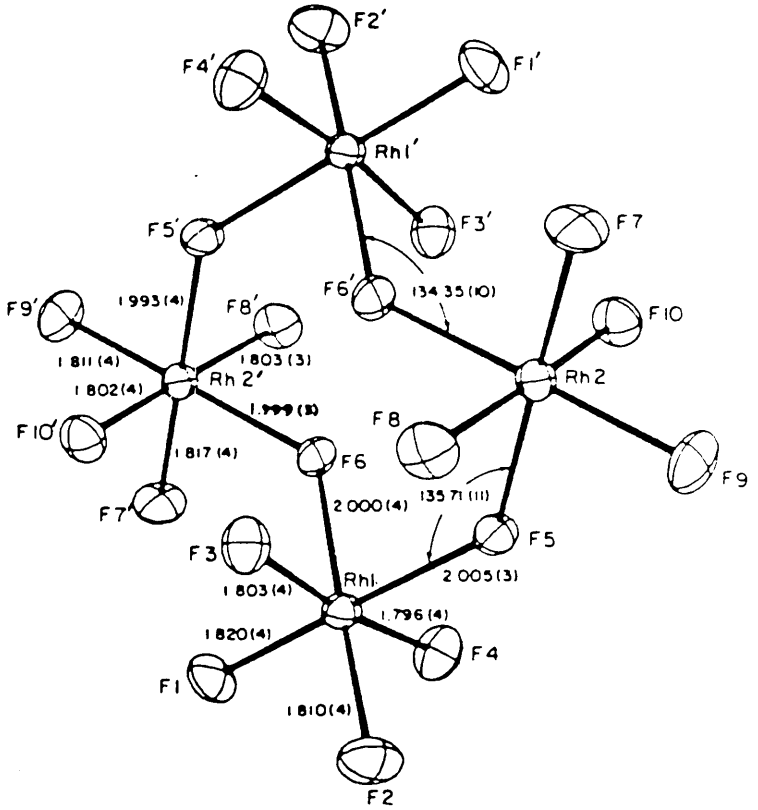
The electron affinity (EA) of a molecule or atom is defined as the difference in energy between the neutral molecule or atom in its ground state, E^o, and the ion in its ground state, E^-, i.e. $EA=E^o-E^-$.[25] There are only a few compounds whose electron



(a) VF_5 (A.J.Edwards)



(b) NbF_5 (A.J.Edwards)



(c) RhF_5 (B.K. Morrell)

Figure 1-1: The molecular units in the three types of transition metal pentafluoride structures.

affinities are accurately known. Measurement of electron affinities is difficult because of the complexity of molecular negative ions.

The electron affinities of 4d and 5d transition metal hexafluorides were calculated by many workers using different methods. Bartlett[26] suggested that a regular increase in electron affinities occurs across the series $WF_6 < ReF_6 < OsF_6 < IrF_6 < PtF_6$. This is in the same direction as the chemical instability of the hexafluorides of this series. From the study of the reactions of NO and FNO with the third row transition metal hexafluorides, Bartlett analyzed the oxidizing properties of the hexafluorides and found that the numerical values of electron affinities increase by approximately 82 kJ mol^{-1} [$EA(ReF_6) > 376$ kJ mol^{-1}, $EA(IrF_6) > 526$ kJ mol^{-1}, and $EA(PtF_6) > 651$ kJ mol^{-1}][25] with unit increase in atomic number of the transition metal. The hexafluoride, PtF_6 has the capability of oxidizing molecular oxygen or xenon.[26]

In 1978, George and Beauchamp[27] determined the electron affinities of WF_6 from ion molecular reactions using ion cyclotron resonance techniques. The F^- anion formed from NF_3 by dissociative attachment, reacts with WF_6 both by an electron transfer reaction and by a fluoride attachment reaction (equations 1-14 and 1-15),

$$F^- + WF_6 \longrightarrow WF_6^- + F \qquad (1\text{-}14)$$

$$F^- + WF_6 \longrightarrow WF_7^- \qquad (1\text{-}15)$$

Reaction (1-14) exhibits a rate constant which decreases with increasing ion energy and thus appears to be exothermic.[28] Reaction of Cl^-, formed from CCl^- by dissociative electron attachment, with WF_6 was not observed, nor was the adduct WF_6Cl^- detected. Therefore, the electron affinity of WF_6 is larger than that of F, and smaller

than that of Cl.

$$EA(F) < EA(WF_6) < EA(Cl) \qquad (1\text{-}16)$$

This suggests that the value of 337 ± 10 kJ mol^{-1} would match the electron affinity of WF_6, because EA(F)=327 kJ mol^{-1} [29] and EA(Cl)=347 kJ mol^{-1}.[30]

Thermochemistry of alkali metal hexafluoromolybdates and hexafluorotungstates was studied by Burgess et al,[31] and the standard enthalpies of formation of some alkali metal (K, Rb and Cs) hexafluoromolybdates and hexafluorotungstates were derived. From these measurements, the gas phase electron affinities of MoF_6 and WF_6 were estimated to be $EA(MoF_6)=517\pm6$ kJ mol^{-1} and $EA(WF_6)=490\pm5$ kJ mol^{-1}.

Although there is some disagreement among the values of the electron affinities for these hexafluorides obtained by different workers, it appears that the electron affinity of MoF_6 is larger than that of WF_6.

1-5-2 Chemical Reactivities of Hexafluorides.

The transition metal hexafluorides are all strong oxidizing agents. The oxidizing abilities of these compounds, in the absence of solvents, increase from left to right for a given series in the periodic table.[32] The second row transition metal hexafluorides are stronger oxidizing agents than their third row counterparts. For example, MoF_6 is a stronger oxidizing agent than WF_6. However, MoF_6 and WF_6 have very similar hydrolytic behaviour and produce oxide fluorides and hydrogen fluoride.

1-5-2a Chemical Reactivities of MoF_6 and WF_6, and Comparisons with Others in the Gas Phase.

(i) Redox behaviour[26,33]

Tungsten hexafluoride is not reduced by nitric oxide, but rhenium and osmium hexafluorides are reduced to the +5 oxidation state.

$$MF_6(g) + NO(g) \longrightarrow NOMF_6(s) \qquad (1\text{-}17)$$

(M=Re, Os)

Furthermore, iridium and platinum are reduced to the +4 or +5 oxidation states depending on the temperature.

$$NO(g) + MF_6(g) \xrightarrow{-20^{\circ}C} NOMF_6(s) \qquad (1\text{-}18)$$

$$2NO(g) + MF_6(g) \xrightarrow{25^{\circ}C} (NO)_2MF_6(s) \qquad (1\text{-}19)$$

(M= Ir, Pt)

In the series from WF_6 to PtF_6, iridium hexafluoride appears to be the only hexafluoride other than PtF_6, to be able to oxidize ONF to release fluorine. Although electron affinities of 5d metal hexafluorides decrease from PtF_6 to WF_6, and WF_6 cannot oxidize NO, the ability of a hexafluoride to accept F^- increases markedly from PtF_6 to WF_6. For example, WF_6 readily adds F^- (equations 1-20 and 1-21),

$$ONF(g) + WF_6(g) \longrightarrow NOWF_7(s) \qquad (1\text{-}20)$$

$$2ONF(g) + WF_6(g) \longrightarrow (NO)_2WF_8(s) \qquad (1\text{-}21)$$

The decrease in F^- acceptor ability along the series from left to right suggests that ligand crowding increases across the series. This accords with the decrease in molecular volume along the series both in the hexafluorides and in the MF_6^- salts.

Similar trends of increasing oxidizing power with increasing atomic number and decreasing molecular volume also occur in the second transition series. In contrast to WF_6, MoF_6 can oxidize NO to give $NOMoF_6$, which indicates that MoF_6 is a stronger oxidizing agent than WF_6.

Like PtF_6, RhF_6 and RuF_6 are capable of oxidizing Xe.[26] Both RhF_6 and RuF_6 are thermally less stable than PtF_6 and both are much smaller than PtF_6.

There is a marked decrease in chemical reactivity through the series chromium hexafluoride, molybdenum hexafluoride and tungsten hexafluoride.[33] The preparation of chromium hexafluoride was reported by Hope et al in 1984, although molecular CrF_6 is thermally unstable and undergoes decomposition to CrF_4 at low pressure.[34] Because of this instability at room temperature, chromium pentafluoride has been studied more widely. It is found that chromium pentafluoride oxidizes the trifluorides of phosphorus, arsenic and antimony. However, only phosphorus trifluoride reduces molybdenum hexafluoride and tungsten hexafluoride and the reduction of tungsten hexafluoride occurs extremely slowly, requiring the presence of anhydrous hydrogen fluoride as a catalyst. So the order of chemical reactivities of these three fluorides CrF_5, MoF_6 and WF_6 appears to be

$$CrF_5 > MoF_6 > WF_6 \qquad (1\text{-}22)$$

It could be predicted that chromium hexafluoride will be chemically more reactive than the thermally stable chromium pentafluoride. Therefore, by extrapolation, chromium hexafluoride will be much more reactive than molybdenum hexafluoride and tungsten hexafluoride.

In the third row transition metal hexafluorides, rhenium hexafluoride is reduced to ReF_5 by PF_3 readily, but it is not reduced

by AsF_3.[35] Selenium tetrafluoride reduces OsF_6 and IrF_6 to quinquevalent derivatives. In contrast to the hexafluorides of osmium and iridium, platinum hexafluoride is reduced to the +4 oxidation state (equation 1-23),[36]

$$PtF_6 + 3SeF_4 \longrightarrow (SeF_4)_2PtF_4 + SeF_6 \qquad (1\text{-}23)$$

Generally speaking, the chemical reactivity of transition metal hexafluorides decreases from the top to bottom, and from the right to left towards WF_6. That is to say, the reactivity decreases as the atomic number increases within a group, and increases as atomic number increases along a row.

(ii) Halogen exchange reactions[37]

Molybdenum hexafluoride and uranium hexafluoride undergo halogen exchange reactions with PCl_3, $AsCl_3$, $SbCl_3$, $TiCl_4$, CCl_4, BCl_3 and PBr_3. On the other hand, WF_6 reacts only with BCl_3, $TiCl_3$ and PBr_3. Molybdenum hexafluoride reacts with all the ionic chlorides of group 1A elements while WF_6 does not react with KCl, RbCl, and CsCl. In these reactions, therefore, MoF_6 appears to be the stronger fluorinating agent and behaves like UF_6 rather than WF_6.

1-5-2b Solution Chemistry of the Hexafluorides MoF_6 and WF_6.

The solution chemistry of transition metal fluorides has attracted considerable interest . A variety of solvents is available and details of the solvents used in this work are discussed in Chapter Three.

Acetonitrile is one of the common solvents used in the study of transition metal fluorine chemistry. A large number of

reactions has been carried out in acetonitrile in this Department.[5] Many 3d and post transition metals are oxidized by the hexafluorides in acetonitrile to give solvated cation, hexafluorometallates(V).[5,8]

In the reaction of Tl and MoF_6 in MeCN, colourless $Tl^{III}(MoF_6)_3.5MeCN$ is isolated when the mole ratio $MoF_6:Tl^{o}$ is high and concentration of MoF_6 is greater than 1 mol dm^{-3}. If these conditions are not used, yellow solids, which may be mixtures of Tl^{I}, Tl^{III} cations with MoF_6^- as the counter anion, are isolated. In these solids the atomic ratio Tl:Mo is always near 1:2.[8] The reaction of WF_6 with Tl metal in MeCN gives a solvated Tl^+ salt.

Molybdenum hexafluoride oxidizes elemental iodine in MeCN at ambient temperature to give bis(acetonitrile)iodine(I)hexafluoromolybdate (V). However, WF_6 has no capability of oxidizing I_2 in this solvent.[38]

In MeCN, WF_6^- and WF_6 react easily to give WF_7^-.[39,40]

$$WF_6(solv.) + WF_6^-(solv) \rightleftharpoons WF_7^-(solv.) + WF_5(solv.) \qquad (1\text{-}24)$$

Alkali metal iodides (A^+I^-) are oxidized by both molybdenum and tungsten hexafluorides in liquid sulphur dioxide to give $AMoF_6$ and AWF_6 according to equations 1-25 and 1-26.[41,42]

$$2AI + 2MoF_6 \longrightarrow 2AMoF_6 + I_2 \qquad (1\text{-}25)$$

$$2AI + 2WF_6 \longrightarrow 2AWF_6 + I_2 \qquad (1\text{-}26)$$

(A = Na, K, Rb and Cs)

In the presence of an excess of an alkali metal iodide, molybdenum hexafluoride is reduced to the hexafluoromolybdate(IV) anion in liquid SO_2.[43]

$$2A[MoF_6] + 2AI \rightleftharpoons 2A_2MoF_6 + I_2 \qquad (1\text{-}27)$$

(A = Li, Na, Rb or Cs)

The potassium salt was obtained impure, mixed with the hexafluoromolybdate(III) salt. The oxidizing ability of some transition metal hexafluorides towards iodine in iodine pentafluoride has been studied.[44] Neither molybdenum nor tungsten hexafluorides oxidize I_2 in IF_5. However, UF_6 and ReF_6 do oxidize I_2 in this solvent. In the UF_6 case, the reaction produces I_2^+ initially at ambient temperature, and when the mole ratio is $UF_6:I_2 > 10:1$ further oxidation of I_2 occurs to give UF_5 and IF_5 (equation 1-28)

$$10UF_6 + I_2 \longrightarrow 10UF_5 + 2IF_5 \qquad (1\text{-}28)$$

A large excess of ReF_6 oxidizes I_2 to I_2^+ in IF_5. These results are consistent with the order of oxidizing ability in IF_5:

$$UF_6 > ReF_6 > MoF_6, WF_6 \qquad (1\text{-}29)$$

The electrochemical properties of MoF_6 and WF_6 have been studied in anhydrous hydrogen fluoride. In 1975, A.M. Bond et al reported that the electrochemical process, WF_6/WF_6^-, was a simple one electron reversible reaction with half-wave potential $E_{\frac{1}{2}}(WF_6/WF_6^-)$ = -0.10V vs. Cu/CuF_2.[45] In 1977, they reported similar work for MoF_6/MoF_6^- in this solvent,[46] and the half-wave potential, $E_{\frac{1}{2}}(MoF_6/MoF_6^-)$, is 0.91V vs. Cu/CuF_2. The half wave potentials of these two couples show that WF_6 is a mild oxidizing agent, since it is reduced at a negative potential (-0.10V) with respect to the Cu/CuF_2 reference electrode. The hexafluoride, MoF_6, is a stronger oxidizing agent since it is reduced at a much more positive potential (0.91V). This is in agreement with the other chemical studies and estimates of the electron affinities for the two hexafluorides referred to above.

Previous work showed that the half-wave potential of MoF_6/MoF_6^- couple in MeCN is 1.60 V, and that of WF_6/WF_6^- is 0.51 V vs.

Ag^+/Ag. The difference of the half wave potentials of these two couples is 1.09 V in MeCN, while it is 1.01 V in anhydrous HF, i.e. in these two solvents the difference is almost the same.

1-5-3 Chemical Reactivities of Molybdenum and Tungsten Pentafluorides.

The chemical reactivity of transition metal pentafluorides increases from left to right across the periodic table. P. Mathur et al reported the electron affinity of MoF_5 to be smaller than that of MoF_6, for example, $EA(MoF_6)=434\pm40$ kJ mol^{-1} and $EA(MoF_5)=318\pm40$ kJ mol^{-1}.[47] H. Dispert et al estimated the electron affinities of WF_6 and WF_5 and found a similar order $EA(WF_6)=357$ kJ mol^{-1} and $EA(WF_5)=121$ kJ mol^{-1}.[48] Tungsten pentafluoride is a considerably better fluoride ion acceptor than molybdenum pentafluoride (ca. 80 kJ mol^{-1} difference).[30] Both MoF_5 and WF_5 show a stronger tendency towards hydrolysis.[49]

1-6 Aim of the Present Work.

The examples described above illustrate that an enormous quantitiy of work has been done in the area of chemical, spectroscopic and electrochemical properties of high oxidation state transition metal fluorides. However, for the lower oxidation state transition metal fluorides, even for the pentafluorides, our knowledge is very incomplete. This is due in part to the lack of satisfactory methods of preparation. Although some preparations have been reported for the lower oxidation state fluorides of early 4d and 5d elements, none of them is very satisfactory. Therefore, the present work is aimed at producing more convenient routes to compounds containing M^V or M^{IV} (M=Mo,W), together with the study of the spectroscopic and

electrochemical properties of these compounds in different non-aqueous solvents.

Previously reported work has shown that the reduction of MoF_6 and WF_6 produces hexafluorometallate(V) salts in MeCN; further reduction of Mo^V and W^V compounds beyond the +5 oxidation state was not observed, although the electrochemical work indicates that MoF_6^{2-} should be accessible.[50] However, in SO_2, hexafluoromolybdate(IV) salts were obtained by the reduction of MoF_6 using alkali metal iodides.[43] Therefore, the reduction of MoF_6^- to MoF_6^{2-} was attempted using Bu_4NI in different solvents.

It is of interest to relate quantitatively the redox properties of reducing agents to those of the oxidizing agents. The relative stabilities of various oxidation states of the heavy transition metals with fluorine ligands have been inferred mainly from qualitative observations. The application of cyclic voltammetry can make the study of the relative oxidizing abilities of these compounds quantitative. In order to compare the redox properties of hexafluoromolybdates and ionic iodides in different solvents, electrochemical studies of these compounds were carried out in different solvents using cyclic voltammetry. There are a number of reports concerning cyclic voltammetry of MoF_6^- salts in MeCN to date. The first cyclic voltammetry measurements on MoF_6/MoF_6^- and WF_6/WF_6^- couples were made by Bond et al in anhydrous hydrogen fluoride solution as described above.[45,46] Now MeCN is a very convenient and conventional electrochemical solvent in which such measurements can be made more easily.

Previously reported work has shown that molybdenum hexafluoride is reduced to molybdenum pentafluoride by molybdenum metal at high

temperature under heterogeneous conditions.[17] Acetonitrile forms isolable 1:1 complexes with some transition metal pentafluorides.[51] Therefore, it should be possible to make 1:1 complexes in one step by the reduction of the metal hexafluorides using their respective metals in MeCN. Thus, the reduction of hexafluorides, MoF_6 and WF_6, by molybdenum and tungsten metals to pentavalent complexes in MeCN at room temperature was carried out.

CHAPTER TWO

EXPERIMENTAL TECHNIQUES.

2-1 Vacuum Line and Glove Box Techniques

Since most of the reactants used and the complexes produced in this work were highly moisture sensitive, therefore, the necessity of using a vacuum line and a glove box throughout the work was inevitable.

Almost all reactions and manipulations were carried out in a conventional Pyrex glass vacuum system. This system, which was constructed with a "Jencons" mercury diffusion pump and an "Edwards High Vacuum" oil pump could provide a vacuum of better than 10^{-3}Torr. Standard, mostly B-14, glass joints were sealed with Apiezon black wax, Voltalef Kel-F or high vacuum Apiezon N grease. Glass stopcocks were used when they were necessary. Most reactions were carried out in Pyrex glass double limb vessels (Figure 2-1) fitted with J. Young or Rotaflo (P.T.F.E/Pyrex) stopcocks and a stainless steel reaction bomb equipped with a stainless-steel needle valve and a brass B-14 cone. All the glassware and reaction vessels were evacuated and degassed thoroughly with a gas-oxygen torch before use.

Non-volatile moisture sensitive compounds were handled in a N_2-atmosphere glove box in which the water level was kept below 10 p.p.m. The glove box was equipped with an evacuable air-lock on one end as a transfer port. This permitted the apparatus and material to be introduced into the glove box without affecting the dry atmosphere condition inside the box. The removal of moisture and oxygen from the box was achieved by circulation over molecular sieves and manganese oxide respectively.

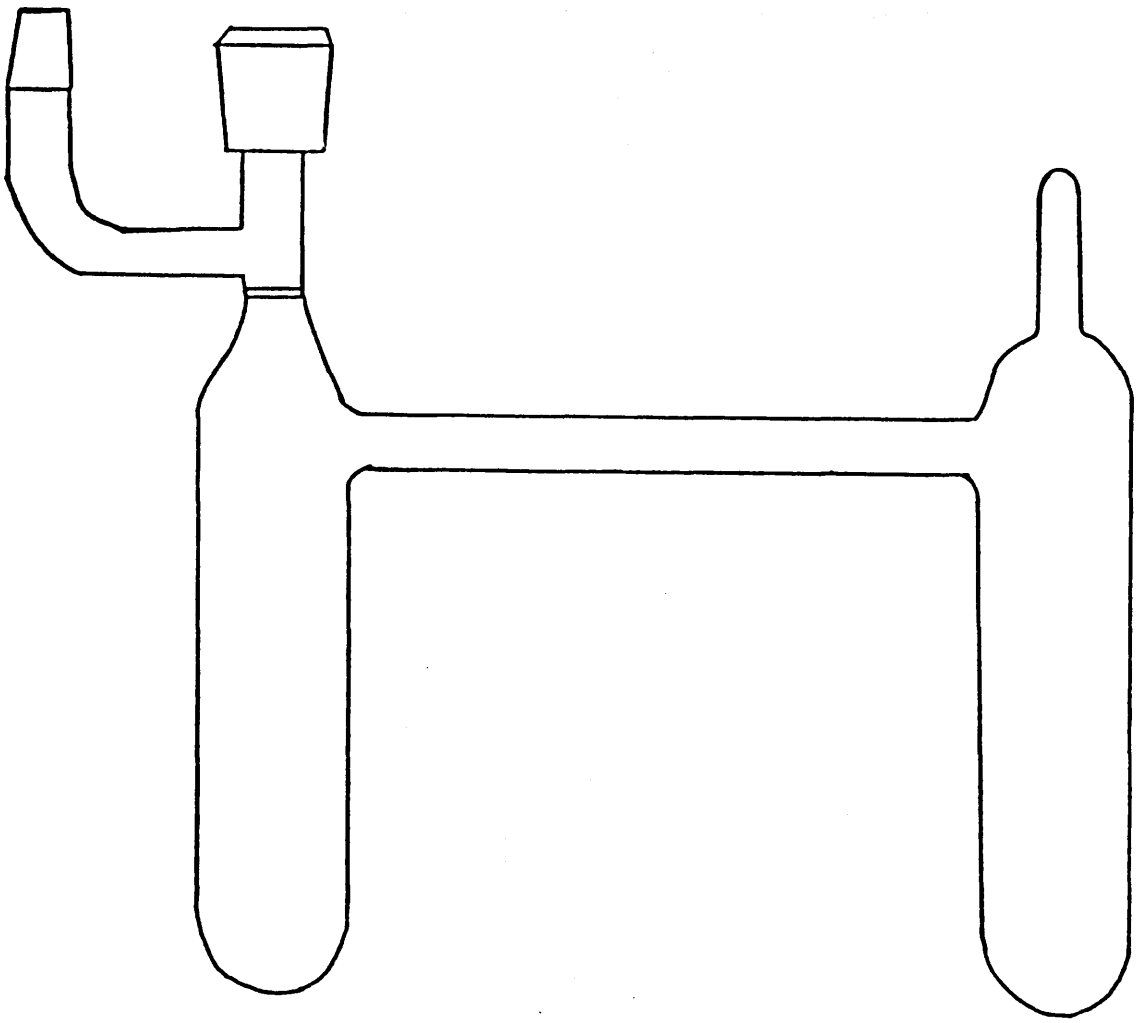


Figure 2-1:Double-limbed reaction vessel

2-2 Electronic Spectroscopy.[52,53]

Electronic absorption spectroscopy is associated with electronic transitions from one state to another in a molecule or transition metal ion. Electronic absorptions usually occur in the visible and ultraviolet regions (10,000 - 50,000 cm^{-1}). In a molecule, electrons occupy different kinds of orbitals, such as σ-bonding, non-bonding and π-bonding, with different energies in the ground state. Electrons from these different orbitals can be excited to higher energy molecular orbitals by absorbing radiation to give rise to many possible excited states.

(1) Ligand Field Spectra

In transition metal complexes, the approach of the ligands to the metal ion causes splitting of the five d-orbitals of the metal. This is called ligand field splitting. When a complex absorbs radiation, an electron can be transferred from a lower energy level orbital to one of the higher energy orbitals. The position of an absorption band in the electronic spectrum depends on the energy of the transition. The absorption bands occur towards the U.V. region of the spectrum with increasing ligand field strength.

Transitions occur according to well documented selection rules. During a transition from the ground state to the excited state, the number of unpaired electrons must be unchanged. Transitions that violate this condition are described as spin or multiplicity forbidden. If the molecule has a centre of symmetry, transitions within a given sub-shell are referred to as

Laporte forbidden. That is to say, in a centro-symmetric molecule, the transition gerade to ungerade, g→u, and ungerade to gerade, u→g are allowed while g→g and u→u are forbidden. For example, transitions p→p and d→d are Laporte forbidden, while the transitions s→p and p→d are allowed. According to the Laporte rule, in perfect octahedral complexes, d→d transitions are not allowed. However, if the ion does not have perfect O_h symmetry, but is distorted so the centre of symmetry is destroyed, the d and p orbitals of the complex are mixed to a certain extent due to hybridization. As a result, transitions between d levels with different amounts of p character can occur. The intensity is roughly proportional to the extent of mixing of the orbitals. A slight distortion can be caused by the normal vibrations for some of the molecules of an octahedral complex at any given time followed by mixing of d and p orbitals unsymmetrically. In this case a very low intensity transition can be observed ($\varepsilon \sim 5$ to 25 $dm^3\ mol^{-1}\ cm^{-1}$). These transitions are said to be vibronically allowed and the effect is described as vibronic coupling. Another possibility is that if the metal-ligand bonding in the complex is largely covalent, the transitions will not be pure 'd-d' but have some ligand character. In addition to these rules, a simultaneous excitation of more than one electron is forbidden.

(2) Charge Transfer Spectra.

Charge transfer transitions are associated with the electronic transitions occurring between molecular orbitals which are essentially centred on different atoms. The charge

transfer transitions occur mostly in the ultraviolet region and the bands are very intense because these transitions are spin and Laporte allowed. For transition metal complexes these spectra involve the transfer of an electron from an orbital centred mainly on the ligand to one centred mainly on the metal atom or vice versa.

Sample Preparation

The vessel used throughout the work was specially designed for obtaining electronic spectra of air-sensitive materials (Figure 2-2). A 10mm Spectrosil cell was attached to a one-limb reaction vessel equipped with a J. Young or Rotaflo stopcock. The reaction could be carried out in the reaction vessel or the sample under investigation could be transferred from other vessels in the glove box. The solution was decanted into the cell and the spectrum was recorded. A second matched cell which contained the pure solvent was used as a reference. Perkin-Elmer Lambda 9 and Perkin-Elmer 550SE UV/vis. spectrophotometers were used to record the spectra.

2-3 Vibrational Spectroscopy.[54,55]

Infrared and Raman spectroscopy were used to determine the presence of coordinated ligands and fluoroanions in the complexes. Infrared spectroscopy was used most frequently in this work. Molecules are promoted to higher-energy excited vibrational states by absorbing radiation from the infrared region of the spectrum.

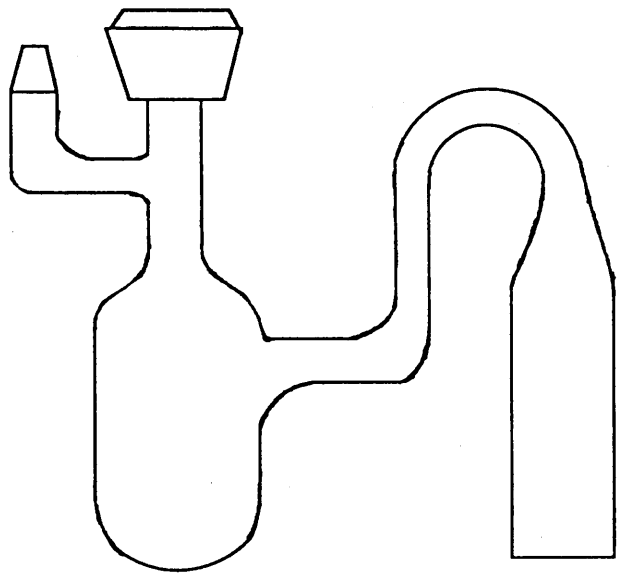


Figure 2-2: Evacuable cell for electronic spectroscopy.

For a vibration of a molecule to be infrared active, the dipole moment of the molecule must change during the vibration. In Raman scattering, the vibrational transitions can also be detected, although the selection rule for Raman spectroscopy is different from that of infrared. Only a molecular vibration which produces a change in polarizability of the species during the vibration is Raman active. Centro-symmetric molecules have no fundamental absorption bands in common between their infrared and Raman spectra. If a common absorption band is found in both the infrared and Raman spectra, the molecule must lack a centre of symmetry. In a polyatomic molecule having a centre of symmetry, the vibrations symmetric with respect to the centre of symmetry are Raman active but infrared inactive, and the vibrations antisymmetric with respect to the centre of symmetry are infrared active but Raman inactive. For example, in octahedral molecules or ions, such as MF_6 or MF_6^- (M = Mo, W or U), the two species T_{1u}, which are antisymmetric with respect to the centre of symmetry, are infrared active while species A_{1g}, E_g and T_{2g}, which are symmetric with respect to the centre of symmetry, are Raman active.

The position of the vibrational absorption bands is related to a force constant which in turn is related to the bond strength. For instance, the force constant of the C≡N stretching vibration in the free MeCN molecule is smaller than that in MeCN which is coordinated to a cation via the lone pair of electrons on nitrogen. As a result, the stretching frequency of the C≡N bond of coordinated MeCN is higher than that of free MeCN molecule.[56,57] The increasing force constant is due to a strengthening of the σ

binding between carbon and nitrogen. In addition to its "S" character, the nitrogen lone-pair orbital will acquire an amount of "P" character upon coordination to Lewis acids. This means an increasing amount of "S" character in the C≡N bond, resulting in an increasing force constant.[58]

In this work, infrared and Raman spectroscopy were used to identify the existence of organic ligands, such as acetonitrile and inorganic anions in the fluoride complexes. The advantage of Raman spectroscopy is that sample preparation does not need special plates, cells or mulling agents. For most air-sensitive complexes, a Pyrex capillary is sufficient. One shortcoming of the Raman technique is that the samples can be decomposed by the laser beam. Fluorides are also inherently weak Raman scatterers. In the infrared technique, there is the problem of hydrolysis of air-sensitive compounds. In order to overcome this problem the mulls were prepared in a glove box using dried mulling agents and the spectra were recorded immediately.

Sample Preparation

For infrared spectroscopy, samples can be examined as gases, liquids, solids or in solution. In the present work, the samples studied were solids. The spectra were recorded over the region 4000 - 200 cm^{-1}. Samples were prepared as mulls. In order to obtain all absorption bands of samples over the region 4000 - 200 cm^{-1}, two mulling agents Nujol and Fluorolube, which have absorption bands at different positions and two different types of plates, AgCl, which is suitable for

4000 - 400 cm^{-1}, and silicon, which is suitable for 400 - 200 cm^{-1} were used. The solid sample (about 1 mg) was first ground to a fine particle size in a small agate mortar and then one or two drops of mulling agent were added. After the sample was dispersed to form a paste, it was pressed between plates of AgCl or silicon and examined as a thin layer. The spectra were recorded using a Perkin-Elmer 983 spectrometer with data station.

Solid samples were prepared in Pyrex glass capillaries for Raman spectroscopy. The Pyrex glass capillaries were sealed to J. Young or Rotaflo stopcocks and degassed on the vacuum line, then loaded with the thin powder of samples in the glove box and sealed on the vacuum line. The spectra were recorded on a Spex Ramalog instrument with either argon ion (488.0, 514.5 nm) or krypton ion (647.1, 520.8, 568.2 nm) laser sources. However, the experiment was unsuccessful because of the decomposition of the samples in the laser beam.

2-4 Cyclic Voltammetry

Cyclic voltammetry is an electrochemical technique used to determine the redox properties of a particular compound in solution. The electric current which flows in the system can be recorded as a function of the applied potential. Cyclic voltammetry is widely used to study the redox properties of compounds or elements and to establish whether these compounds or elements can be readily oxidised or reduced.

A voltammogram can be described as the variation of

current with applied potential (Figure 2-3).

Figure (2-3) illustrates a one electron reduction, but the same interpretation can be applied in reverse for an oxidation step. As the applied potential becomes more negative, the current increases slowly from the starting point A to B. This is the residual current which is caused by a condenser current, that results from the charging of a double layer at the electrode surface, and a diffusion current, due to the presence of traces of oxidisable or reducible material in the solution. At the point B, near the electrode potential of the electroactive species, the reduction of the species begins; as a result the current rises sharply to C, at which point the reduction is complete.

In this process, the electroactive species approach the electrode by diffusion. After the applied potential passes the point which corresponds to C towards the more negative direction, the current rises slowly again due to the residual current. The current vs. voltage plot therefore has a wave-like form.

Further chemical reactions usually affect the reversibility of electroactive species. For a reversible wave, the half-wave potential, $E_{\frac{1}{2}}$, which corresponds to the potential at the position of half way up the curve, equals the formal electrode potential, E^{o}, $E_{\frac{1}{2}} \approx E^{o}$. For a non-reversible wave the half-wave potential is not equal to the formal electrode potential, therefore the system must be tested for reversibility.

The non-reversibility of some waves is caused by further

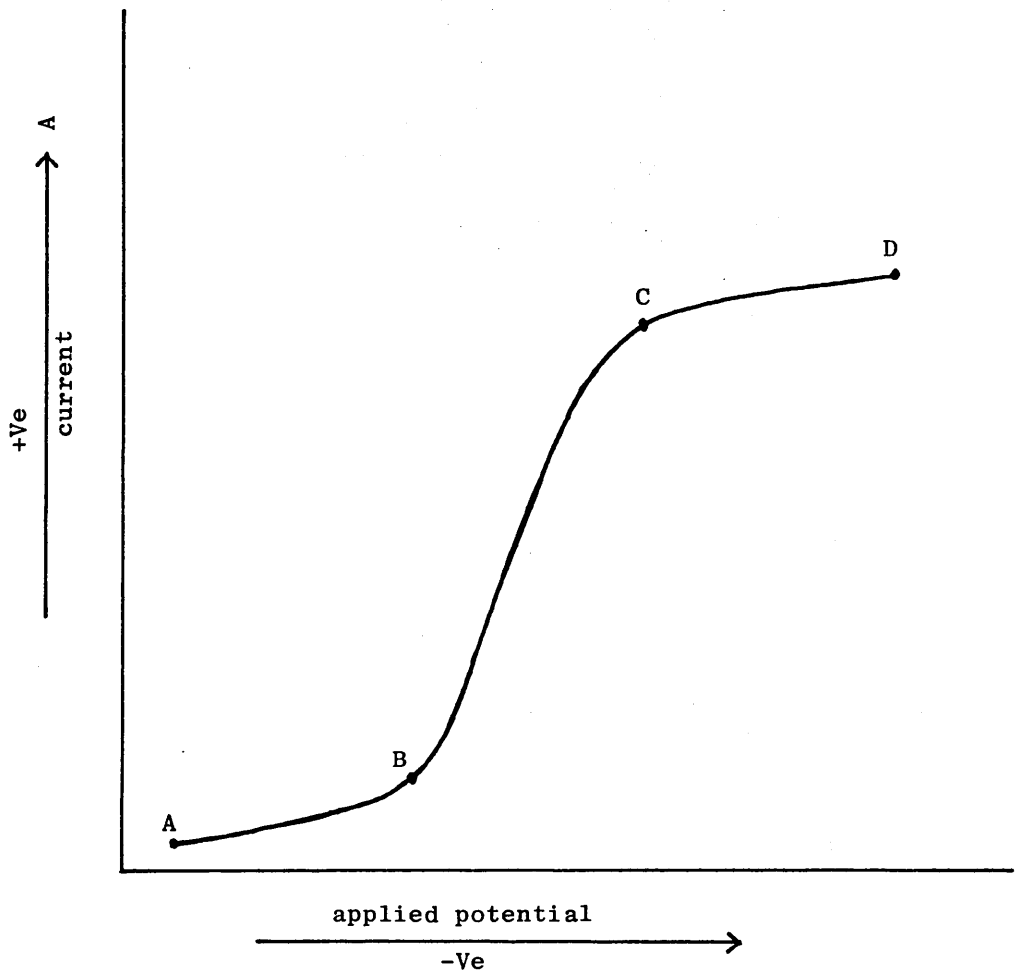


Figure 2-3: Current vs. applied potential

chemical reaction in which one of the species in the couple is involved. For example, in the following process:

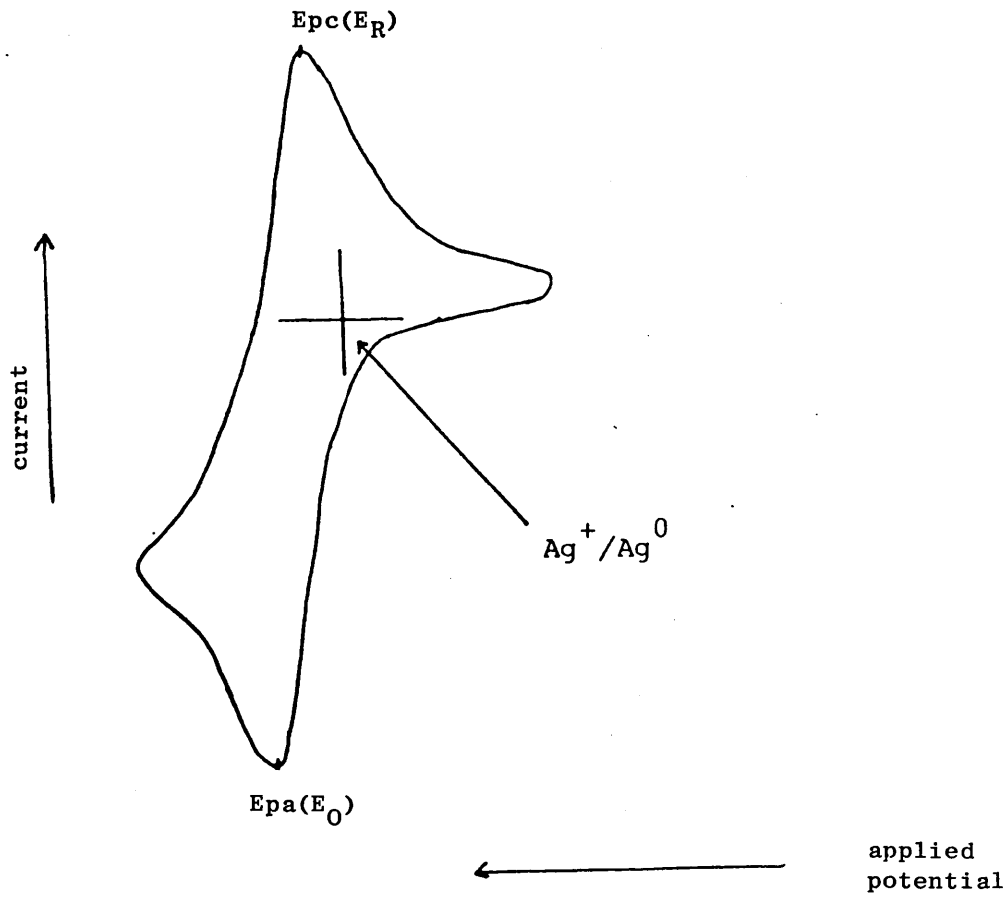
$$A \longrightarrow B^{+} \longrightarrow C^{+}$$

A is oxidized electrochemically to produce B^{+} which proceeds via a chemical reaction to produce C^{+}. The reduction potential of C^{+} will be different from that of B^{+} and as a result the wave will be non-reversible.

In cyclic voltammetry, the potential of the working electrode is changed at a constant rate, backwards and forwards between limits. These limits should be adjusted to lie within the voltammetric range of the solution.

The cyclic voltammogram of Cp_2Fe^{+}/Cp_2Fe in acetonitrile is a typical reversible one-electron redox process (Figure 2-4).

The decrease of the surface concentration of the oxidized form at the electrode and the increase in concentration of the reduced form are both potential dependent. The compound starts to be reduced as the applied potential becomes increasingly negative, hence the current increases as a function of the applied potential to a maximum peak called the cathodic peak (Epc). At the cathodic peak the electrode surface concentration of oxidized form is negligible compared with the concentration of the reduced form. After the cathodic peak, the concentration gradient and the charge flux both decrease. A reverse phenomenon occurs in the opposite potential direction and results in another peak called the anodic peak (Epa) at which the electrode surface concentration of the reduced form is negligible compared



$$\frac{E_0 + E_R}{2} = E_{1/2}$$

Figure 2-4: Cyclic voltammogram of $(\eta^5\text{-}C_2H_5)_2Fe$.

with that of oxidized form.

The following equations can be used for a reversible system:[59]

$$E_R = E_{\frac{1}{2}} - \frac{0.0285}{n} \text{ V} \qquad (2\text{-}1)$$

$$E_O = E_{\frac{1}{2}} + \frac{0.0285}{n} \text{ V} \qquad (2\text{-}2)$$

where E_R and E_O are the potentials of the reduction and oxidation peaks respectively, $E_{\frac{1}{2}}$ is the half-wave potential and n is the number of electrons transferred. The waves obtained for a rapid electron transfer process which is followed by slow chemical reaction are sometimes called quasireversible waves.[60] The quasireversible waves will be apparent in the cyclic voltammogram. In this case, the height of the cathodic peak is larger than that of the anodic peak when the starting material is the oxidised form of the couple, and vice versa for the reduced form.[61] From the magnitude of the peak to peak separation between anodic and cathodic peaks, a distinction between quasireversible and reversible processes can be made. For a reversible system, the peak to peak separation for a one electron process is 57 mV.[59]

$$E_O - E_R = 57\text{mV} \qquad (2\text{-}3)$$

This peak to peak separation for a quasireversible system is greater than 57 mV. In an irreversible process, one half of a redox couple will be totally involved in a chemical reaction. For example, if all the reduced form of a couple is involved in

a chemical reaction during the process, then the anodic peak will be absent. That is to say, all the reduced form produced by the electrochemical process is used in the reaction and as a result it is not available for oxidation on the return sweep.

Electrochemical Cell for Cyclic Voltammetry

Two different types of electrochemical cell were used in this work. One of the cells which is designed for studying the cyclic voltammetry of air-sensitive compounds at room temperature is shown in Figure 2-5. This cell consists of three electrodes, reference, working and auxiliary electrodes. The reference electrode is a silver wire dipping into 0.1 mol dm^{-3} $AgNO_3$ in MeCN solution. Both the working and auxiliary electrodes are platinum wires (1.0mm diameter). All the electrode wires are vacuum sealed through the glass by spot welding to tungsten wire and sheathing the assembly in uranium glass. The cell contains three compartments, reference, bridging and working, made from 24 and 10-15 mm diameter tubing and joined by B14 and B19 greaseless 'O' ring joints. Connections to vacuum and to storage ampoules for reference, bridging and working compartments and for addition of solvent are by polytetrafluoroethylene (P.T.F.E), Pyrex stopcocks. The reference, bridging and working compartments are connected using unfired Vycor tips joined to glass by heat shunk P.T.F.E. tubing.

The other cell used in this work is designed for studying the electrochemical properties of air-sensitive compounds at low temperature (Figure 2-6). The cell consists of a central

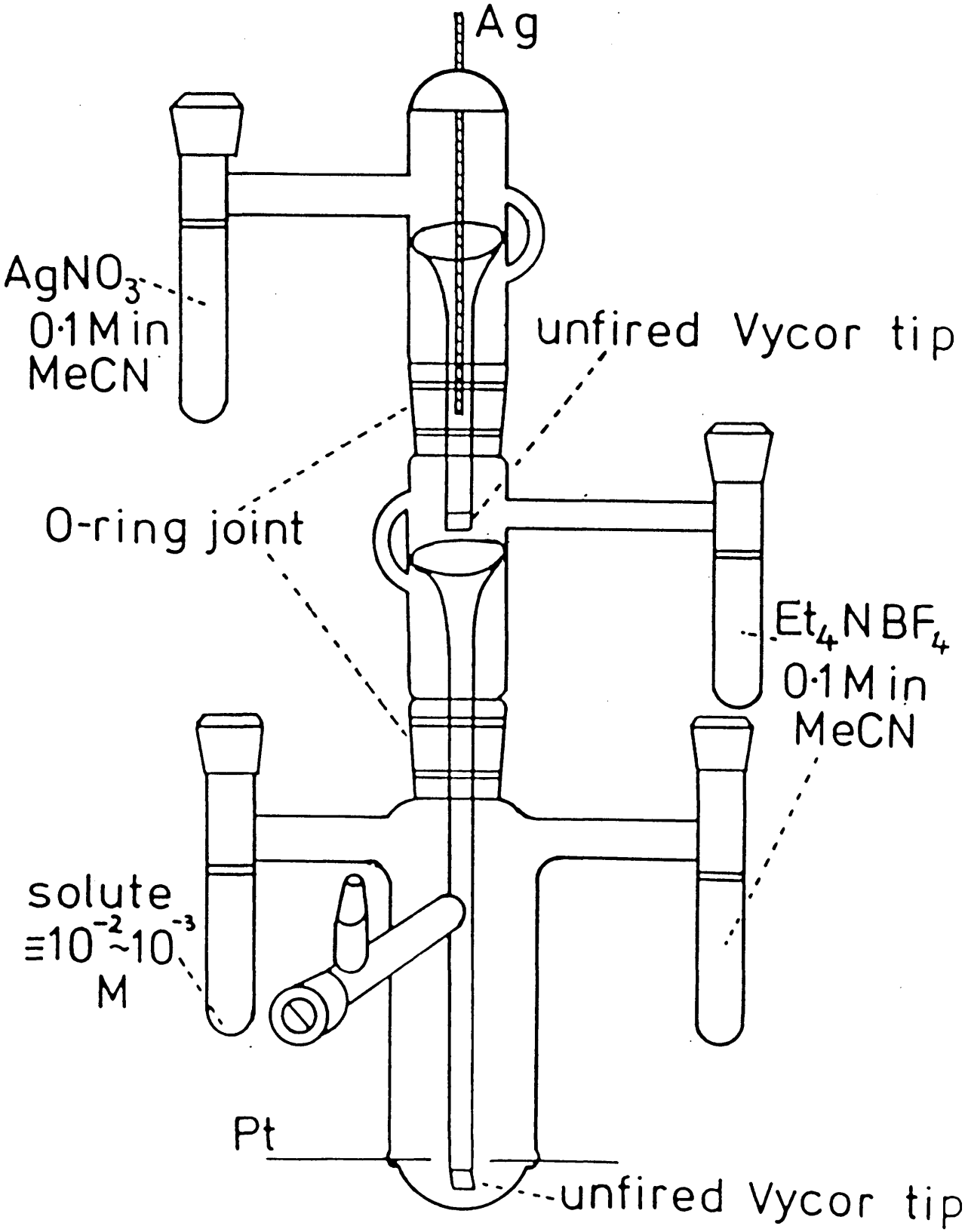


Figure 2-5: Electrochemical cell for room temperature cyclic voltammetry.[8]

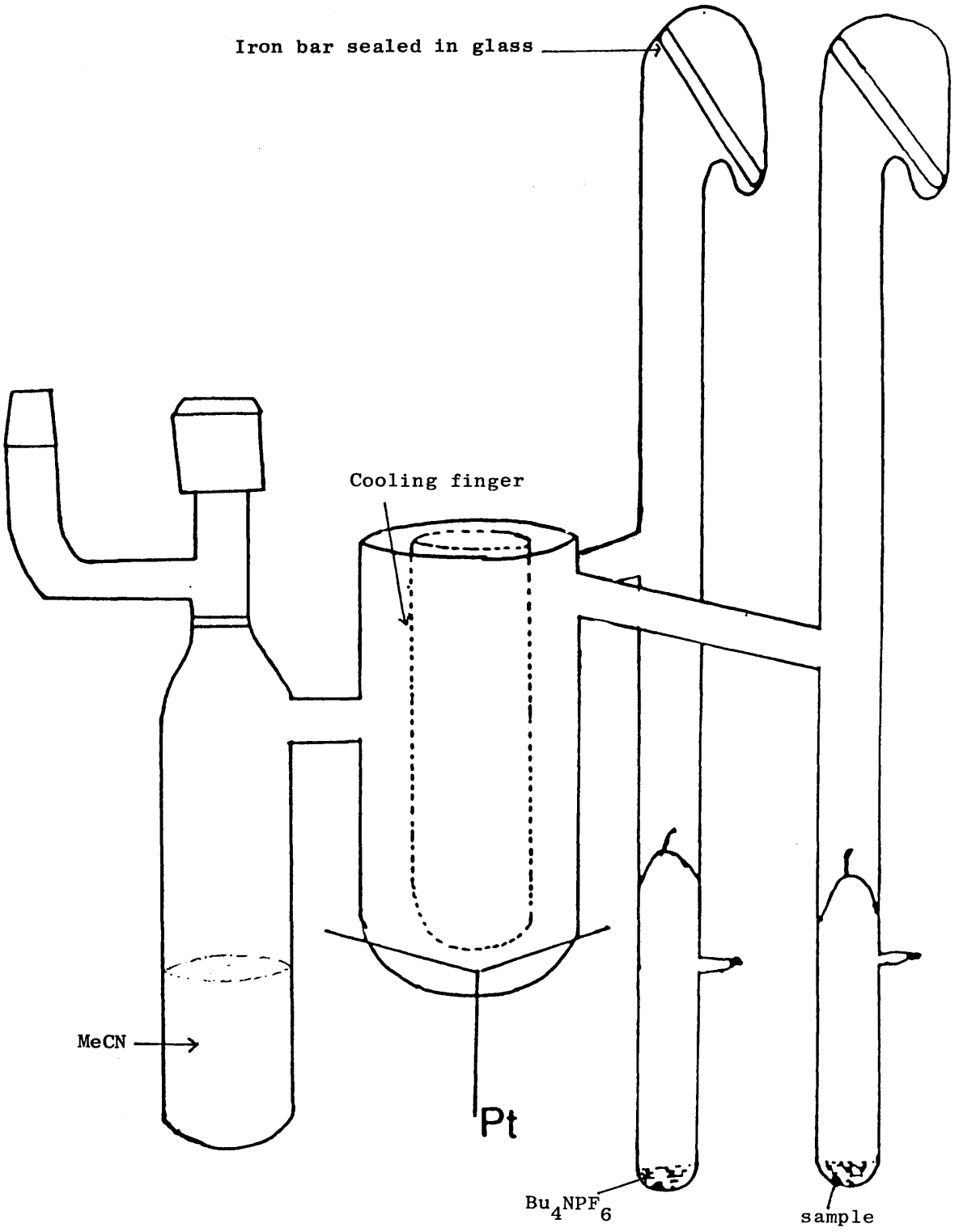


Figure 2-6: Electrochemical cell for low temperature cyclic voltammetry.[62]

main body with two electrodes (working and auxiliary electrodes) and a cooling finger, two sidearms with the storage ampoules for electrolyte and solute to be studied and a front Rotaflo compartment for vacuum manipulation and solvent transfer. An internal reference is necessary in this cell, and ferrocene was used in this work.

Solvent and Electrolyte

The solvent and the electrolyte play important roles in electrochemical experiments.

An ideal solvent should have minimal interaction with the compound which is being studied and the electrolyte system. The necessary interaction of the solvent with the solute and the electrolyte is that the solvent should dissolve the solute and the electrolyte, but there must not be a chemical reaction among them. The solvent must be purified rigorously before it is used. The purification procedures will be described later. The solvent should be stable towards redox processes over a wide potential range. Low melting points are essential for low temperature experiments. Three different solvents, acetonitrile, dichloromethane and sulphur dioxide were used in this work.

Supporting electrolytes are used to decrease the electrical resistance of the solution, and to ensure that the movement of the electroactive species is by diffusion not by electrical migration in the voltage field across the cell. There should be minimal interaction between electrolytes and other components in the solution. In order to carry the bulk of the current efficiently

the electrolyte $[A]^+[B]^-$ should dissociate in the solvent, but there must not be any reaction among the electrolyte, solute, and the solvent. The supporting electrolyte must be stable towards redox processes over a large potential range, and be free from impurities which might react with the species under investigation. Tetra-n-butylammonium hexafluorophosphate (Bu_4NPF_6) was used as the supporting electrolyte in the present work. The potential range of Bu_4NPF_6 has been found to be from +3.0V to -2.6V vs. Ag^+/Ag in MeCN, from +2.9V to -3.2 V vs. the Pt quasi reference electrode in CH_2Cl_2 and from +3.0 to -0.5 V vs. the Pt quasi reference electrode in SO_2.

Preparation of the Electrolyte

The electrolyte Bu_4NPF_6 used in this work was prepared by the reaction of Bu_4NOH and KPF_6 in water (equation 2-4).

$$Bu_4NOH + KPF_6 \xrightarrow{H_2O} Bu_4NPF_6 + KOH \qquad (2\text{-}4)$$

The white crystalline precipitate obtained was suction filtered and washed with distilled water many times until the pH of the washings reached 7.0. The electrolyte Bu_4NPF_6 was dried under vacuum, and then dissolved in CH_2Cl_2 and the solution was filtered to recrystalize the solute. This process was repeated until Bu_4NPF_6 became crystal clear. The CH_2Cl_2 was removed by rotary evaporation at 40-45°C each time, and then pumped on the vacuum line overnight at room temperature. The Bu_4NPF_6 was stored in the glove box ready for use.

Preparation of Solutions

For room temperature cyclic voltammetry studies, the solutions were prepared by the following method. The cell was evacuated and degassed on the vacuum line, and the compound to be studied was sealed in a frangible ampoule under vacuum. The cell and the sealed ampoule were transferred to the glove box and the reference ampoule of the cell was loaded with silver nitrate solution (2 cm^3, 0.1 mol. dm^{-3} in MeCN). The electrolyte solution (2 cm^3 and 8 cm^3, 0.1 mol. dm^{-3} in MeCN respectively for bridging and working compartments) and the sealed frangible ampoule containing the compound were loaded into their respective ampoules. The cell was re-evacuated and the solutions were degassed then tipped into their respective compartments.

The cell was connected to a potentiostat and a XY recorder. After the working potential range of the electrolyte was determined, the frangible ampoule was broken, the compound was dissolved in the solution, and its voltammogram was recorded immediately. The scan rate, current amplification factor and the voltage scale factor were varied depending upon the species which was under investigation. Usually faster scan rates were required for species which would undergo irreversible reaction in the time scale of a lower scan rate study.

For low temperature cyclic voltammetry studies, the low temperature cell was loaded as follows. Two breakseal tubes were evacuated and flamed out on the vacuum line and transferred into the glove box. One of them was loaded with the compound (0.005 mmol) and the other was loaded with electrolyte(1 mmol). The tubes were degassed, sealed and joined to the side arms of

the cell (Figure 2-6). The internal reference material, sealed in a frangible ampoule, was loaded into the front Rotaflo compartment. The solvent was distilled into the Rotaflo compartment. The glass seal of the tube containing electrolyte was broken by a glass-sheathed iron bar. The electrolyte was dissolved in the solvent and the solution was tipped into the working compartment. After the working potential range of the electrolyte solution had been determined, the seal of the tube containing the solute was broken, the compound was dissolved and its voltammogram was recorded. At the final stage, the frangible ampoule containing the reference material was broken, the reference material was dissolved in the solution, and the voltammogram was recorded again.

The cyclic voltammograms were recorded using a Princeton Applied Research Model 173 Potentiostat/Galvanostat, linked to a LLOYD 'XY' plotter, and a Model 175 Universal Programmer.

2-5 Magnetic Susceptibility

The magnetic moments of the Mo^{V} complexes prepared in this work were determined by the Gouy method.

The magnetic properties of a substance are essentially determined by the properties of its electrons. If all the electrons of a substance are paired, its magnetic moment will be zero. Such substances are called diamagnetic. This property is due to small magnetic moments that are induced by the magnetic field but do not exist in the absence of the field. When

diamagnetic substances are placed in an applied field, this field will induce a small moment in these materials and this moment is opposed to the external field. As a result, these substances will be repelled by the external field. If there are electrons remaining unpaired, the substance will have a resultant magnetic moment. Such substances are called paramagnetic, and are attracted by a magnetic field. The paramagnetic moment is inherent and exists in the absence of an external field. Its magnitude depends mainly on the number of unpaired electrons.

In the Gouy method, the compound is loaded in a cylindrical tube, whose volume is known, and hung from a microbalance between the poles of the magnet. Paramagnetic substances are attracted by the magnetic field which increases the weight of the sample, whereas diamagnetic substances are repelled, causing a decrease in weight. The force (F) on a sample in the magnetic field is given by

$$F = g\Delta W = \tfrac{1}{2}(\kappa - \kappa_{air})H^2A \qquad (2\text{-}5)$$

where g is a constant (981 dynes s^{-2}), ΔW(g) is the change in weight, κ and κ_{air}(c.g.s. units) are the volume susceptibilities of the sample and air respectively, H(Oersted) is the magnetic field and A is the cross section area of the sample. H^2A can be calculated by using a substance of known volume susceptibility (κ). Therefore by calculation of H^2A and measuring F of a compound, the volume susceptibility can be calculated. The relation between the gram magnetic susceptibility, χ(cm^3 g^{-1}), and the volume susceptibility, κ, of the compound is shown by the

following equation

$$\chi = \kappa/\rho \qquad (2\text{-}6)$$

where ρ (g cm^{-3}) is the density of the sample. The gram susceptibility, χ, is converted to the molar susceptibility χ_m (cm^3 mol^{-1}) by the relationship (equation 2-7),

$$\chi_m = \chi M \qquad (2\text{-}7)$$

where M is the gram formula weight.

In order to obtain the magnetic moment of the metal ion alone, a diamagnetic correction is required for other elements in the molecule,

$$\therefore \quad \chi_m^{corr} = \chi_m - \text{diamagnetic correction.}$$

Since the diamagnetic corrections are negative,

$$\therefore \quad \chi_m^{corr} > \chi_m$$

The effective magnetic moment, $\mu_{eff.}$, of the metal ion is given by the equation (2-8),

$$\mu_{eff.} = 2.84 \sqrt{\chi_m^{corr}.T} \quad (B.M.) \qquad (2\text{-}8)$$

where T is the temperature in Kelvin.

Experimental Procedure

A known volume of cylindrical glass tube, sealed at one end and fitted with a glass quickfit stopper, was filled with the sample in the glove box. All measurements were made using a CAHN TA 450 microbalance and a Newport 1½" electromagnet type C.

A standard material, mercury tetra(thiocyanato)cobaltate(II) ($HgCo(NCS)_4$; χ = 16.64 x 10^{-6} C.g.S. at 20°C) was used to calculate H^2A and the value obtained was used in equation (2-5) to determine 'κ' of the compound. Another standard material of known magnetic moment, manganese(III) tris(acetylacetonate), $Mn(acac)_3$, was used to check the correct operation of the equipment. The magnetic moment of $Mn(acac)_3$ was found to be 4.99 B.M. at 20°C. (Literature value is 4.95 B.M).[63]

2-6 Atomic Absorption Spectroscopy.[54,64]

This is an important technique for the analysis of many elements. The method is based upon the absorption of electromagnetic radiation by atoms. When a beam of light from a discrete source of radiation is passed through a flame containing the sample in the form of an atomic vapour, part of the radiation is absorbed and part transmitted. The absorbance, A, can be expressed by the Beer Lambert Law (equation 2-9).

$$A = \log \frac{I_o}{I_t} = \varepsilon lc \qquad (2\text{-}9)$$

where I_o is intensity of incident light. I_t is intensity of transmitted light. ε is a constant related to the absorption, l(cm) is the path length of the flame, C (atom cm^{-3}) is the concentration of atoms in the flame. In equation (2-9), if ε and l remain constant, the absorbance is directly proportional to the concentration of the atoms in the flame C, so under ideal conditions it is directly proportional to the concentration of the sample solution.

Sample Preparation

Analyses for molybdenum in MoF_5.NCMe were performed by this technique in the present work. Sample solutions for atomic absorption spectroscopy were prepared as follows. The compound (about 40-60 mg) to be analysed was sealed in a frangible ampoule to prevent decomposition before the analysis. The external surface of the ampoule was washed with acetone and dried thoroughly and the ampoule was weighed precisely. The ampoule was then broken over a filter funnel leading to a 100 cm^3 beaker into which the contents of the ampoule were quantitatively transferred. Both the ampoule and the funnel were washed with 'Analar' HNO_3 (5 cm^3) to remove any residues using a Pasteur pipette. The ampoule and the funnel were rinsed with distilled water (10 cm^3), and the washings were added to the beaker without any loss. To obtain the exact weight of the compound taken, the broken glass was dried in the oven and weighed precisely. The resulting solution was heated gently just below its boiling point for 30 minutes. After the solution was cooled to room temperature it was transferred quantitatively to a 100 cm^3 volumetric flask and distilled water was added to bring the total volume of the solution to 100 cm^3.

An aliquot (10.00 cm^3) of this solution was transferred to another 100 cm^3 volumetric flask and diluted to 100 cm^3. This solution was used in the subsequent analytical measurement. In this final dilution Na_2SO_4 (1.0 g dm^{-3}) was added to minimise interference effects in the N_2O-C_2H_2 flame.

Calibration was carried out by aspirating a series of

standard solutions ranging from 10 ppm to 50 ppm. These solutions were prepared by serial dilution of 1000 ppm 'Spectrosol' molybdenum, which is dissolved in HCl, standard solution (B.D.H. Chemical Ltd). The sample and standard solutions were matrix matched with respect to HNO_3 and Na_2SO_4 concentrations. A Perkin-Elmer 370 A Atomic Absorption Spectrophotometer with a nitrous oxide-acetylene flame was used for the measurements.

2-7 Purification of Solvents.

Three solvents, acetonitrile, dichloromethane and sulphur dioxide were used extensively throughout this work. It was necessary that solvents for the synthetic and electrochemical work should be free from all oxidizable and reducible impurities, therefore purification was necessary in each case. Purification of these solvents was relatively simple, and the procedures are briefly described here.

Purification of Acetonitrile.[65]

A number of methods have been used by different workers for purification of MeCN. The method applied in this Department is an extension of the method of Walter and Ramelay.[66] It consists of a series of refluxes of HPLC Grade 'S' MeCN (Rathburn Chemicals Ltd) followed by rapid distillation in a Pyrex still equipped with a 0.75m silvered vacuum jacketed separating column. The following sequence of reagents was used; quantities and times are given in parentheses:

(a) Anhydrous $AlCl_3$ (15 g dm^{-3}; 60 min)

(b) $KMnO_4$ + Li_2CO_3 (both 10 g dm^{-3}; 15 min)

(c) $KHSO_4$ (15 g dm^{-3}; 60 min)

(d) CaH_2 (20 g dm^{-3}; 60 min)

(e) and (f) P_2O_5 (1 g dm^{-3}; 30 min)

The solvent was distilled rapidly after each reflux topping and tailing by approximately 3%. During distillation and reflux, the solvent was protected from atmospheric moisture by a silica gel drying tube. At the final step, MeCN was transferred directly from the still to vessels containing activated Al_2O_3 (neutral, 60 mesh) without exposure to atmospheric moisture, and degassed on the vacuum line at least three times. Finally MeCN was transferred to storage vessels containing previously activated 3A molecular sieves by vacuum distillation. Acetonitrile purified in this way, had an absorbance of 0.1 (H_2O reference) at 200 nm and an apparent U.V. cut-off at about 175 nm.

Purification of Dichloromethane

The purification of dichloromethane was achieved by refluxing analytical grade CH_2Cl_2 over P_2O_5, using a Pyrex still protected from atmospheric moisture by a silica gel drying tube. The solvent was refluxed twice over P_2O_5 for about 20 min in each case. The solvent was then transferred, without exposure to the atmospheric moisture, to degassed Pyrex vessels. It was then degassed on the vacuum line three times and stored over Linde type 4A molecular sieves[67] in vessels wrapped with aluminium foil. Purified CH_2Cl_2 had an absorbance

at 255 nm of < 0.15 (H_2O reference) and a U.V. cut-off point at about 230 nm.

Purification of Sulphur Dioxide

The purification of SO_2 consisted of shaking sulphur dioxide (B.D.H) with P_2O_5 at about -40°C. A vessel fitted with a Rotaflo stopcock was quickly loaded with P_2O_5 in the air, and pumped for a short time on the vacuum line. The vessel containing P_2O_5 was transferred to the glove box and the P_2O_5 was divided into three parts and added to three previously evacuated and flamed out vessels. The vessels were attached to the vacuum line and re-evacuated. The solvent was distilled from the cylinder to one of the vessels, and shaken, then transferred to the second vessel by vacuum distillation, and shaken again. Finally the solvent was degassed and stored in the third vessel over P_2O_5 at -196°C for use.

2-8 Preparation of Molybdenum and Tungsten Hexafluorides.[10]

The hexafluorides were prepared by the direct fluorination of the powdered metals with elemental fluorine at 300-350°C.

The procedure and apparatus for the preparation of molybdenum hexafluoride and tungsten hexafluoride used in this work were identical. In this chapter, the preparation of molybdenum hexafluoride is described.

Since molybdenum hexafluoride (m.p. = 17.4°C, b.p. = 35°C) is a toxic, highly hygroscopic material, it must be handled in a

clean, dry, high vacuum system.

The apparatus, Figures 2-7 and 2-8, consists of a 60 cm long nickel tube equipped with Swagelok couplings, glass apparatus and a small nickel boat.

Pure molybdenum powder (5 g) was placed in the small nickel boat and spread as much as possible. The boat containing the molybdenum metal was placed inside the tube. The Swagelok coupling was then replaced. The tube was placed in a furnace and glass apparatus, which contained NaF in traps E, F, G and I, was attached to the tube using the Swagelok couplings and P.T.F.E. ferrules. The apparatus was then attached to the fluorine gas cylinder on the one side and linked to a vacuum line with Kel-F grease via B-14 sockets on the other side, Figure 2-9.

After the apparatus was evacuated (10^{-2} torr), the glass section of the apparatus was degassed several times over a period of 2 hours and NaF was activated, by heating with a medium flame from a gas-oxygen torch.

Once the apparatus had cooled to room temperature, the stopcock A, was closed and nitrogen gas was admitted very slowly into the system to bring it to atmospheric pressure. The joint, B, was separated and N_2 flow (70 cm^3 min^{-1}) continued for approximately 12 hours.

The furnace was switched on before the admission of F_2, in order to achieve a reaction temperature of about 320^{o}C. Meanwhile the traps C (for trapping moisture from the air), G (for collecting product MoF_6), and I (for trapping trace HF) were

cooled to -80°C, using dry ice/dichloromethane slush baths.

The fluorine cylinder was then opened, and the cylinder head pressure gauge was adjusted to 40 psi. Then the fluorine was passed through the system diluted with N_2 to give a 1:2 ratio by volume of fluorine/nitrogen and a tube flow rate of 100 cm^3 min^{-1}. The product was collected in trap G and after approximately one hour the reaction should be completed. Testing for F_2 at the exit of the apparatus can be accomplished by the use of potassium iodide/starch indicator paper.

When the reaction was complete, the main valve of the fluorine cylinder,6, was closed. After the cylinder pressure gauge had dropped to zero, valves 5 and 4 were closed. Nitrogen was then flushed through the system for about 15 minutes.

The glass apparatus was sealed at point H and immediately after, the collection train (b) was separated from trap (a), the collection train (b) was attached to a vacuum line to be evacuated, the product being frozen in liquid nitrogen. The product MoF_6 was purified by trap to trap vacuum distillation firstly from G to F and then from F to E. To obtain a pure product a slow distillation was necessary at this stage, from -80°C to -196°C. The main impurity is usually $MoOF_4$ which is less volatile. Finally, the product was sealed in E at the point O and stored at -196°C.

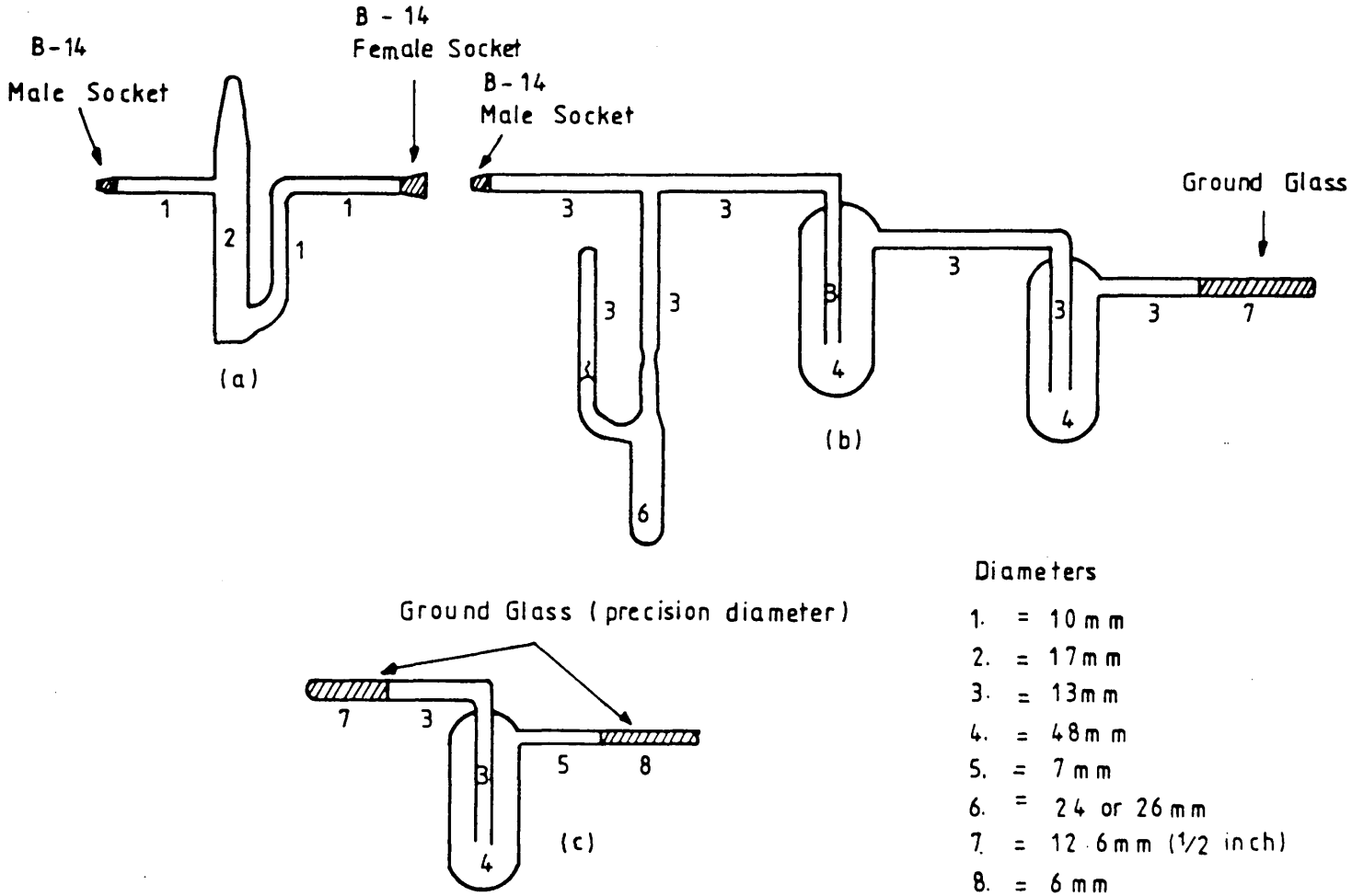
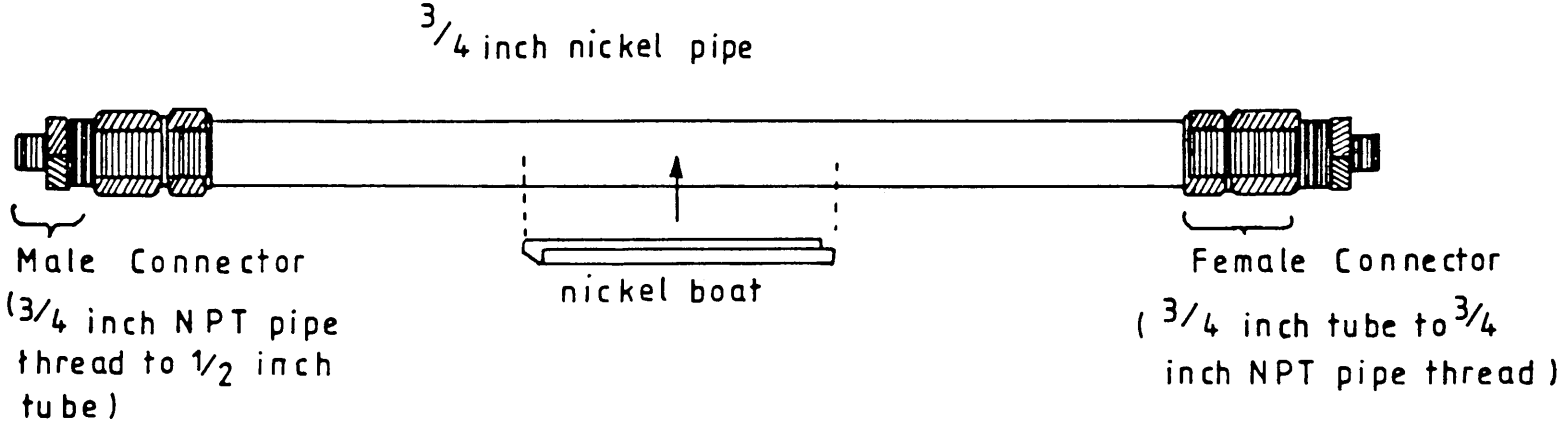


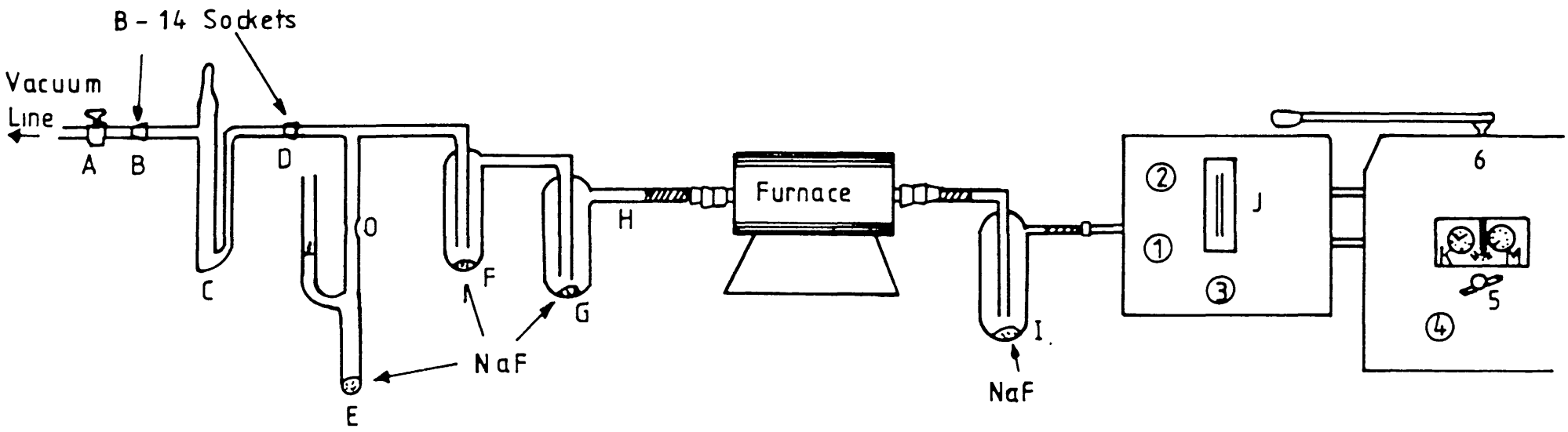
Figure 2-7 GLASS APPARATUS.



※ BOTH CONNECTORS ARE STAINLESS STEEL. (316)

NICKEL TUBE & BOAT

Figure 2-8



FLUORINATION SYSTEM FOR MoF_6

Figure 2-9

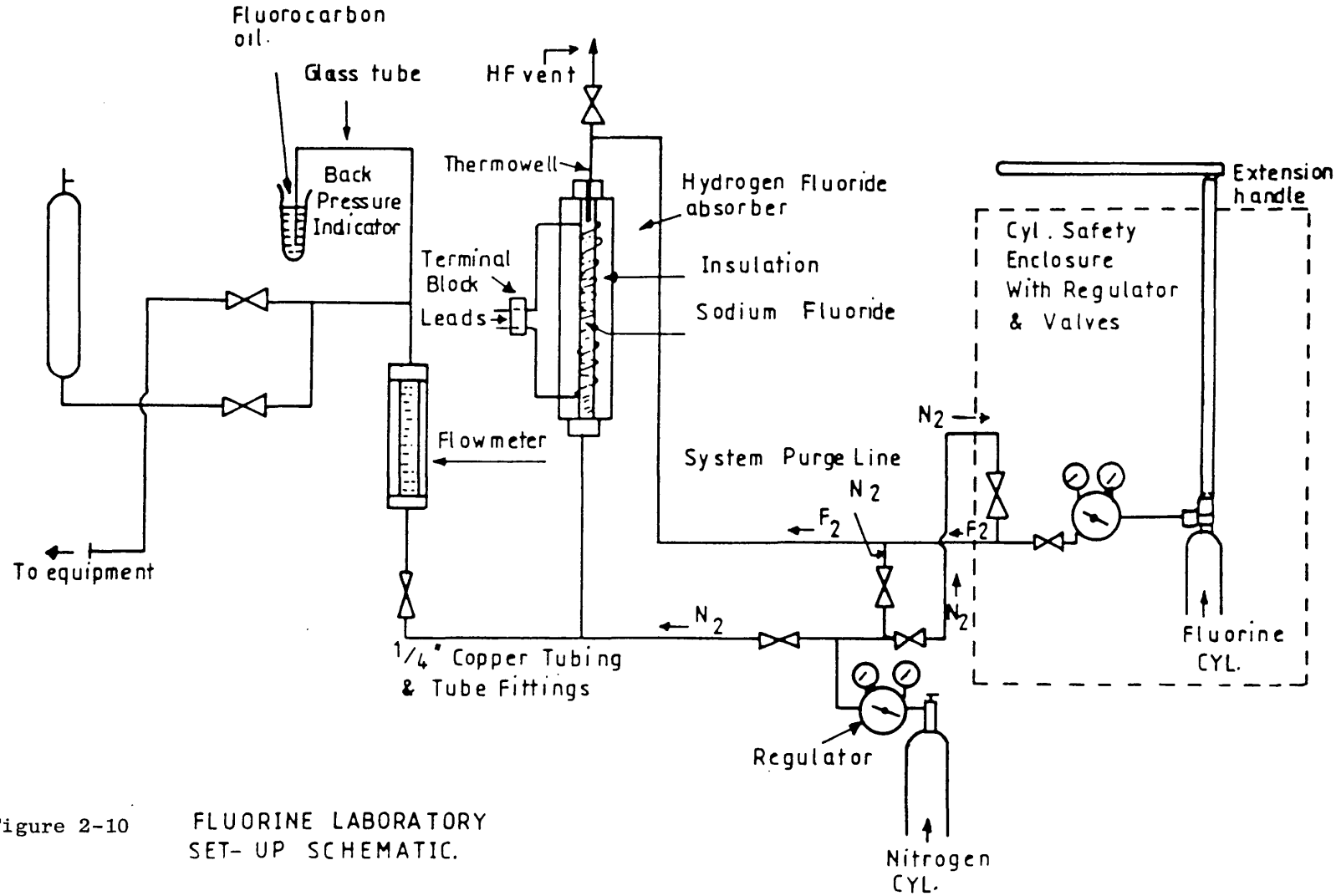


Figure 2-10 FLUORINE LABORATORY SET- UP SCHEMATIC.

2-9 Preparation of MoF_5.[17]

Molybdenum pentafluoride was prepared by the reaction of molybdenum hexafluoride with powdered molybdenum metal at 150°C.

$$Mo + 5MoF_6 \xrightarrow{150^{\circ}C} 6MoF_5 \qquad (2\text{-}10)$$

Since molybdenum pentafluoride is a very hygroscopic compound, it must be handled either in a vacuum line or in a dry box.

A brief description of the preparation is as follows. A Hoke bomb equipped with a stainless-steel needle valve and B-14 Monel cone was used in the preparation. The bomb and the valve were first checked to ensure that they were leak-tight. The bomb was transferred to the glove box. The needle valve was removed and high-purity molybdenum powder (1.0g) was added to the bomb. The needle valve was replaced and the reaction bomb was attached using Kel-F grease to the vacuum line adjacent to a break sealed vessel which contained MoF_6. The reaction bomb was evacuated and degassed at about 150°C over a period of 12h using an oil bath, and the glass section of the line was degassed with a gas-oxygen torch. The lower section of the reaction vessel was cooled to -196°C and MoF_6 (about 12.0g) was condensed into the bomb. Then the needle valve was closed and the mixture was heated with the oil bath at 150°C for 24h.

The reaction bomb was set up in conjunction with the apparatus shown in Figure 2-11. The pentafluoride could be separated from unreacted MoF_6 using this apparatus.

The glass collection vessel was carefully degassed with the gas-oxygen torch, meanwhile the reaction bomb was cooled to

room temperature. The section B of the apparatus was cooled to -196°C. The reaction vessel was opened at the needle valve, and the large amount of unreacted MoF_6 was immediately collected in the section B. Then the bomb was slowly warmed to 100°C, and yellow MoF_5 appeared in section B. After about 2h at this temperature, a small quantity of MoF_5 was collected in section B. This procedure was carried out under dynamic vacuum. The apparatus was isolated from the pump, the lower section of the reaction bomb was cooled to -196°C and section B was warmed to -80°C with a dry ice/dichloromethane slush bath to distil unreacted MoF_6 back into the bomb. The MoF_5 remained in the section B, which was sealed at constrictions C and D. Repetition of the reaction of unreacted MoF_6 with Mo metal led to a further small quantity of MoF_5 being obtained but some MoF_6 still remained unchanged.

The apparatus shown in Figure 2-12 was used to separate the small quantity of MoF_6 from MoF_5. Section E was cooled to -196°C, meanwhile section G was warmed to -80°C in a dry ice, CH_2Cl_2 slush bath to collect MoF_6 in section E. After all the MoF_6 was collected, the apparatus was sealed at the constriction H, and the MoF_6 was stored for further use. Section F was cooled to -196°C, and the section G was slowly warmed to 100°C. The MoF_5 was collected in the section F under dynamic vacuum. The apparatus was sealed at constrictions I and J, and stored at -196°C for use.

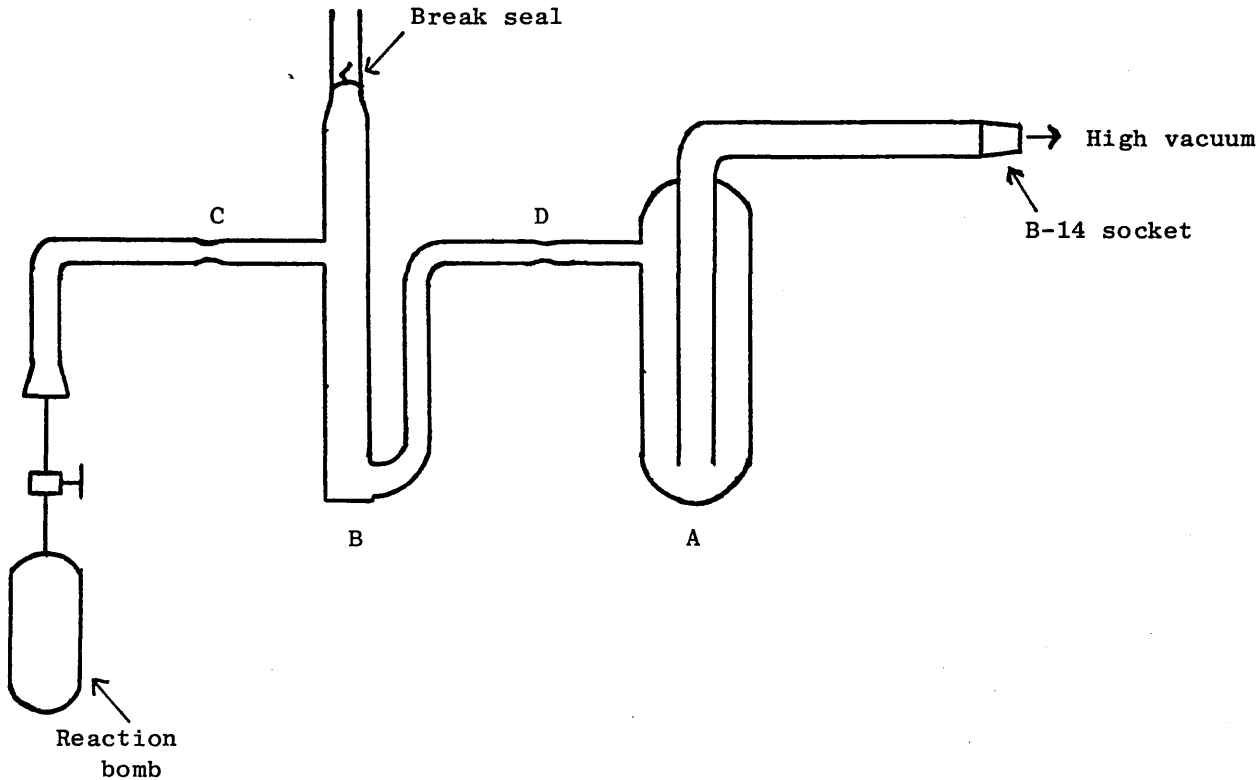


Figure 2-11: Apparatus for collection of MoF_5

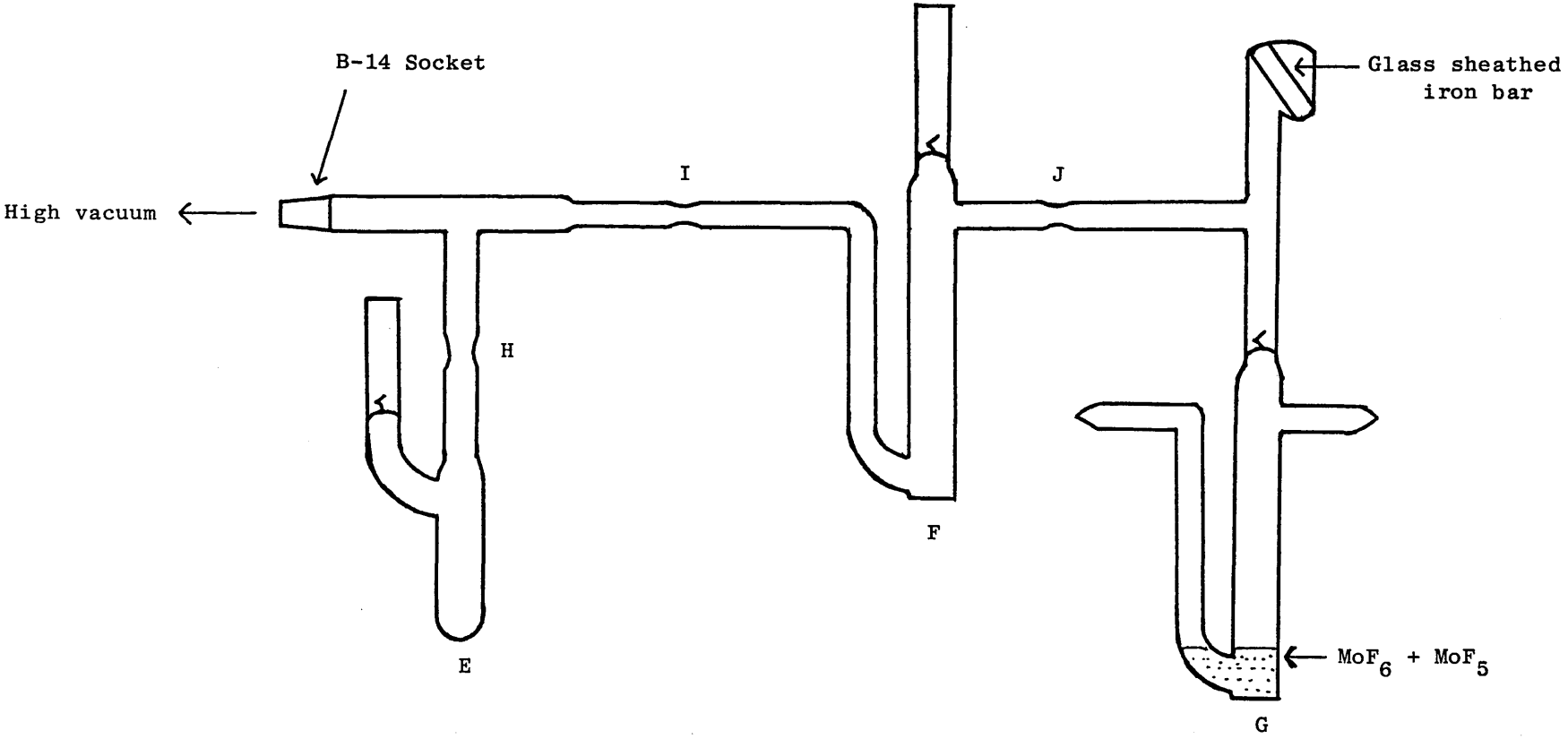


Figure 2-12: Apparatus for separation of MoF_6 and MoF_5

CHAPTER THREE

REACTION OF IONIC IODIDES WITH MOLYBDENUM AND TUNGSTEN HEXAFLUORIDES.

3-1 INTRODUCTION

3-1-1 Lewis Acid-Base Reactions

G.N. Lewis[68] proposed a definition of acid-base behaviour in terms of electron-pair donation and acceptance. The Lewis acid-base definition is the most widely used of the acid-base definitions because of its simplicity and wide applicability. Lewis defined a base as an electron-pair donor and an acid as an electron-pair acceptor. That is to say, a basic substance has a lone pair of electrons which may be used to complete the stable group of another atom, and an acidic substance can employ a lone pair from another molecule in completing the stable group of its own atoms.

Acetonitrile interacts with strong Lewis acids, the pentafluorides of Sb, As, Nb, Ta and Mo, to give isolable 1:1 complexes.[65] Most pentafluorides act as Lewis acids. Amongst the non-metal pentafluorides the strongest acidity is found in those of group VB elements. The strength of the acidity increases down the series PF_5, AsF_5 and SbF_5.[69]

A large number of Lewis acid-base reactions have been carried out in MeCN using chloride species as reagents. The solvated metal cations of M(II) (M = Mn, Fe, Co, Ni, Cu), are formed from the reaction of the metal(II) chlorides with $TlCl_3$, $FeCl_3$, and $AlCl_3$ in MeCN. The anions formed are $FeCl_4^-$, $TlCl_4^-$ and $AlCl_4^-$.[70] Similarly Lewis acid-base reactions involving covalent high oxidation state fluorides as Lewis acids and metal binary fluorides as Lewis bases have been carried out to generate solvated metal cation salts in MeCN, for example, anhydrous CuF_2

reacts with the pentafluorides of Ta, P and As to generate solvated Cu^{II}, hexafluoroanion salts at ambient temperature in MeCN[71] (equation 3-1).

$$CuF_2(s) + 2MF_5(solv.) \longrightarrow Cu^{2+}(solv.) + 2MF_6^-(solv.)$$

(M = Ta, P, As) (3-1)

These reactions suggest that MeCN has good solvating properties and that the pentafluorides have strong fluoride ion acceptor properties. The compounds TaF_5 and AsF_5 are generally regarded as stronger Lewis acids than PF_5, and in MeCN exist as monomeric MF_5NCMe complexes.[51,72,73,74] Copper(II) fluoride reacts with tungsten hexafluoride in acetonitrile to give solvated copper(II) heptafluorotungstate(VI), $[Cu(MeCN)_5][WF_7]_2$. The hexafluorotungstate(V) anion behaves as a fluoride-ion donor in MeCN and reacts with WF_6 to give the WF_7^- anion as one product.[40] In contrast to complex chloroanions, complex fluoroanions generally show little or no tendency to coordinate to a cation, leaving only the solvent in its primary coordination sphere. Thus the metal cation and anion are separated by the solvent.

3-1-2 Solvents

A large number of solvents is available for the study of the non-aqueous solution chemistry of transition metal fluoride complexes. For example, protonic solvents such as hydrogen fluoride,[75] dipolar aprotic solvents, for example acetonitrile[65] or liquid sulphur dioxide,[43] and non-polar solvents such as dichloromethane have been used as non-aqueous solvents by many workers.

Three solvents were used in the present work and are described below.

(i) Liquid Sulphur Dioxide[76]

Sulphur dioxide is a dipolar, aprotic, solvent which possesses the ability to promote ionization of some covalent solutes. Some physical properties of SO_2 are: m.p. = -75.52°C, b.p. = -10.08°C, dielectric constant of the liquid: 22.3 (-60°C), 20.0(-40°C) and 15.4 (0°C). Compared with MeCN, the lower dielectric constant of liquid sulphur dioxide indicates that its ionizing capabilities will be limited; this is borne out by the generally higher solubilities of covalent compounds in SO_2 and solubilities of ionic compounds are generally low. For the alkali metal halides, decreasing lattice energies are accompanied by increasing solubility. Tetraalkylammonium salts which have small lattice energies are, in general, quite soluble in liquid SO_2. The unusually high solubility of iodide salts is due to additional factors. The polarizability of the large multielectron iodide ion is quite large so that the dispersion energy is a significant contribution to the solvation energy.

Liquid sulphur dioxide is predominantly an acceptor solvent. Therefore, electron-donor molecules and anions are more strongly solvated than electron acceptors or cations. Since these properties are unique among commonly used solvents, liquid SO_2 is quite useful as a synthetic reaction medium and as a solvent for the study of a variety of solvation phenomena.

(ii) Acetonitrile

Acetonitrile has several advantages for the study of the reactions of metal cations. Its physical properties,[65]

m.p. = -40°C, b.p. = 81.6°C, and high vapour pressure enable it to be manipulated easily in vacuo. Its relatively large liquid range enables reactions to be carried out at varying temperatures. It has a relatively high dielectric constant,[65] 37.5 at 25°C, therefore, it is a good solvent for the study of ionic compounds. Acetonitrile has a good donor ability through the lone pair of electrons on nitrogen, and is a strong enough Lewis base to solvate a large number of cations and a good ligand to coordinate to the central atom in many complexes. The purification of acetonitrile is relatively simple.[65] The purified solvent has a working electrochemical potential range of 5.7V. It is transparent in the visible region and in the U.V. region up to 175 nm. Because of these properties, acetonitrile is an approved solvent for synthetic and electrochemical work and with the availability of CD_3CN, it is excellent solvent for spectroscopic work.

The role of acetonitrile as a donor solvent and the nature of its coordination to the metal centre has been reviewed.[77,78] Coordination by the donation of the lone pair of electrons on nitrogen results in an increase in the stretching frequencies of the C≡N and C-C bonds compared with the free molecule.[56] This is due mainly to the enhancement of the stretching force constant of the sigma band in the CN system which results from a shortening of the C≡N bond.[57] This increase in the vibrational stretching frequency of the C≡N bond is very important evidence for the presence of coordinated MeCN.

(iii) Dichloromethane[79]

Some of the physical properties of CH_2Cl_2 are similar to those of MeCN, for example, it has a large liquid range (m.p. = -97°C, b.p. = 40°C), and high vapour pressure (400 torr at 24°C). However, its dielectric constant (9.08 at 20°C) is low. Dichloromethane has been used as a solvent for electrochemical studies of transition metal halides.[80]

Purified CH_2Cl_2 is transparent in the visible and in the U.V. region down to 230 nm, so it is a reasonably good solvent for spectroscopic work. However, the solubilities of many ionic compounds, for example, alkali metal iodides, are very low, and this limited its use in the present work.

3-1-3 The Behaviour of Iodine in MeCN, CH_2Cl_2 and SO_2.

Iodine dissolves readily in a number of organic solvents such as MeCN, CH_2Cl_2 and CCl_4 or in some inorganic solvents, for example, SO_2, to give slightly different coloured solutions depending on the nature of the solvent. For example, a solution of iodine in MeCN is brown while iodine in CH_2Cl_2 is pink. In the electronic spectra of these solutions, the absorption band due to I_2 appears at a different position in different solvents (Table 3-1).

Table 3-1 Electronic spectra of I_2 in MeCN and CH_2Cl_2

	MeCN (λ_{max} nm)	CH_2Cl_2 (λ_{max} nm)
I_2	450	505

This colour difference may be explained in terms of a donor-acceptor interaction leading to complex formation between the solvent (donor) and iodine (acceptor) which influences the optical transition energy. Iodine forms charge transfer complexes with electron donor solvents. The most direct evidence for the formation of a complex $L \rightarrow I_2$, in solution comes from the appearance of an intense charge transfer band in the near ultraviolet region.[81] The iodine absorption band shifts towards higher energy under the interaction of a basic solvent, for example MeCN, because of the formation of charge transfer complexes.[82]

Unlike the situation in IF_5, molybdenum hexafluoride oxidizes elemental iodine in MeCN at ambient temperature to give a solvated iodine(I) compound.[83] Acetonitrile is a moderately weak base and has a good solvating ability to stabilize this monovalent iodine(I) cation and disproportionation reactions do not occur. In liquid sulphur dioxide, iodides such as alkali metal iodides are oxidized by MoF_6 and WF_6 to release elemental iodine and no further oxidation is reported to occur. On the other hand, further reduction of MoF_6^- to MoF_6^{2-} by excess of alkali metal iodides has been reported as described in Chapter One.[43]

One of the earliest recognized polyiodide anions is I_3^- whose formation accounts for the increased solubility of I_2 in water on addition of KI. In CH_3CN, the stability of I_3^- is substantially high. In liquid SO_2, the addition of iodine increases the conductivity of potassium and rubidium iodides, and the addition of these electrolytes also increases the solubility of iodine in SO_2. These effects are a maximum at a ratio of iodide

to iodine of 1:1, indicating formation of I_3^-.[76]

Iodide salts have high solubilities in liquid sulphur dioxide, and can be strongly solvated by the solvent. It is suggested that the charge transfer transition in the anion - SO_2 interaction gives rise to the intense yellow colour of these solutions.[76]

3-1-4 Preparation of Hexafluoromolybdate(V), (IV) and Hexafluorotungstate(V) Salts.

The chemistry of the reduction of MF_6 (M= Mo, W) to MF_6^- salts has been extensively studied. Early research work was carried out in liquid SO_2.[41] The preparation of hexafluoromolybdate(IV) salts was also carried out in SO_2 later as mentioned above.[43] The reaction proceeds in two steps according to equations 3-2 and 3-3:

$$2AI + 2MoF_6 \longrightarrow 2AMoF_6 + I_2 \qquad (3\text{-}2)$$

$$2AMoF_6 + 2AI \rightleftharpoons 2A_2MoF_6 + I_2 \qquad (3\text{-}3)$$

(A = Li, Na, Rb or Cs)

However, many preparations of MoF_6^- and WF_6^- salts have been carried out also in acetonitrile. Molybdenum and tungsten hexafluorides oxidize the transition and post-transition metals Ag, Tl, Pb, Zn, Cd, Hg, Mn, Co, Ni and Cu in acetonitrile at ambient temperature to give MoF_6^- and WF_6^- salts of solvated cations.[5] Other preparations of MoF_6^- and WF_6^- salts in this solvent were

described in Chapter One.

The work described in this chapter was aimed at the examination of the redox behaviour of MF_6 and MF_6^- salts (M = Mo, W) towards different ionic iodides in CH_2Cl_2 and SO_2 solvents to increase the routes available for the preparation of hexafluorometallates of M^V and M^{IV}.

3-2 Results and Discussion.

3-2-1 The Reactions of MoF_6 and WF_6 with Ionic Iodides in SO_2.

Tetra-n-butylammonium iodide reduces MoF_6 in liquid sulphur dioxide rapidly at -60°C to produce a dark brown solution from which dark grey solid is obtained after the removal of the volatile materials, solvent, unchanged MoF_6 and iodine. The solid product, which is very sensitive to moisture, becomes very pale yellow when it is washed with the solvent several times. The infrared spectrum of the solid contains two strong bands at 635 cm^{-1} and 250 cm^{-1}, which should be assigned to the ν_3 and ν_4 vibrations of the hexafluoromolybdate(V) ion respectively (Table 3-2). The assignment of the bands due to the MoF_6^- anion was made by comparison with the previous work.[84]

The infrared spectrum of the MoF_6^{2-} salt contained absorption bands at 540 (vibration ν_3) and 255 cm^{-1} (vibration ν_4).[43] The bands corresponding to these vibrations appeared at 741 and 262 cm^{-1} for MoF_6 [85] and at 635 and 250 cm^{-1} for MoF_6^- [84] (Table 3-3).

Table 3-2 Infrared Spectrum of Bu_4NMoF_6 and Bu_4NWF_6 in the Solid State (Reaction in SO_2).

Bu_4NMoF_6 $\nu_{max}(cm^{-1})$	Bu_4NWF_6 $\nu_{max}(cm^{-1})$	Bu_4NI $\nu_{max}(cm^{-1})$	Assignment [a]
1033 m	1038 m	1030 m	$(C_4H_9)_4N^+$ band
930 m	932 m	925 m	" "
883 m	885 m	883 m	" "
740 m	745 m	738 m	" "
635 s			$\nu_3(MoF_6^-)$
	595 s		$\nu_3(WF_6^-)$
250 s			$\nu_4(MoF_6^-)$
	240 s		$\nu_4(WF_6^-)$

s - strong m - medium

[a] The bands due to $(C_4H_9)_4N^+$ were assigned by comparison with previous work[86] and by comparison with the i.r. spectrum of Bu_4NI.

Table 3-3 The Vibrations ν_3 and ν_4 in Infrared Spectra for MoF_6, MoF_6^- and MoF_6^{2-}.

Vibrations	MoF_6	MoF_6^-	MoF_6^{2-}
$\nu_3(cm^{-1})$	741	635	540
$\nu_4(cm^{-1})$	262	250	255

Tungsten hexafluoride reacts with Bu_4NI readily in SO_2 at -60^oC. The procedure and observations were very similar to those described above for Bu_4NI and MoF_6 in SO_2. The resulting pale yellow product is very sensitive to traces of moisture and immediately became blue when it was exposed to atmosphere. The solid state i.r. spectrum showed the presence of the Bu_4N^+ cation and contained two strong bands at 595 cm^{-1} and 240 cm^{-1}, which were due to the characteristic vibrations ν_3 and ν_4 for the WF_6^- anion (Table 3-2).

The reactions of NaI and KI with MoF_6 in SO_2 at -60^oC are rapid. The iodides NaI and KI are reasonably soluble in liquid SO_2 at low temperature (-60^oC). When the reactants are mixed, I_2 is released and the complex fluoride is precipitated. Using a large excess of MoF_6, all of the alkali iodide reacts, and the product obtained is colourless after the removal of the volatile materials under high vacuum by washing with the solvent several times. The solute is very sensitive to moisture, and contains bands which can be assigned to the MoF_6^- anion (Table 3-4).

Similarly, both NaI and KI react readily with WF_6 in liquid SO_2, although these reactions were a little slower than the corresponding reactions involving MoF_6. The observations are essentially identical to these made previously by Peacock and coworkers.[41]

3-2-2 The Reactions of MoF_6 or WF_6 with Ionic Iodides in CH_2Cl_2.

Tetra-n-butylammonium iodide is soluble in CH_2Cl_2, but the alkali metal iodides NaI and KI are insoluble. The compound, Bu_4NI, reacts rapidly with molybdenum hexafluoride in CH_2Cl_2 to produce a dark pink solution at room temperature. From this solution, a dark grey soluble solid was isolated by vacuum distillation of the volatile materials, CH_2Cl_2, unchanged MoF_6, and I_2. After the solid product was washed with CH_2Cl_2 several times, the colour of the solute became very pale yellow. The product is very sensitive to moisture and rapidly becomes blue when it is exposed to moist air. Its solid state i.r. spectrum contains two strong characteristic bands due to the MoF_6^- anion at 635 cm^{-1} and 250 cm^{-1}. It also contains bands due to the presence of the Bu_4N^+ cation (Table 3-5).

The iodine released during the reaction was identified by its electron absorption band at 505 nm in CH_2Cl_2.

Tungsten hexafluoride is also reduced readily by Bu_4NI in CH_2Cl_2 at room temperature to give a pale yellow product, which is very hygroscopic. The presence of the cation, Bu_4N^+, and the anion WF_6^- were identified by i.r. spectroscopy (Table 3-5). The electronic spectrum of the volatile pink solution contained a band at λ_{max} = 505 nm confirming that iodine is released in the reaction.

The iodides, NaI and KI are insoluble in CH_2Cl_2, and for this reason the reaction of NaI with MoF_6 and KI with MoF_6 are very slow in CH_2Cl_2 at room temperature. Reactions involving NaI appear to be faster than those of KI, however both reactions were

Table 3-4 Infrared spectra of $NaMoF_6$ and $KMoF_6$ in the solid state (Reaction in SO_2)

$NaMoF_6$ $\nu_{max}(cm^{-1})$	$KMoF_6$ $\nu_{max}(cm^{-1})$	Assignment
635 s	635 s	$\nu_3(MoF_6^-)$
250 m	250 m	$\nu_4(MoF_6^-)$

s = strong m = medium

Table 3-5 Infrared spectrum of Bu_4NMoF_6 and Bu_4NWF_6 in the solid state (Reaction in CH_2Cl_2)

Bu_4NMoF_6 $\nu_{max}(cm^{-1})$	Bu_4NWF_6 $\nu_{max}(cm^{-1})$	Bu_4NI $\nu_{max}(cm^{-1})$	Assignment
1033 m	1038 m	1030 m	$(C_4H_9)_4N^+$ band
930 m	932 m	925 m	" "
883 m	884 m	883 m	" "
740 m	745 m	738 m	" "
635 s			$\nu_3(MoF_6^-)$
	595 s		$\nu_3(WF_6^-)$
250 s			$\nu_4(MoF_6^-)$
	240 s		$\nu_4(WF_6^-)$

s = strong m = medium

incomplete. The interaction of these compounds produces a pink solution and a brown colour on the surface of the solid. The electronic spectrum of the volatile pink material shows a band at 505 nm due to I_2. The brown solids, although insoluble in CH_2Cl_2, are soluble in MeCN giving rise to deep brown solutions. In the case of KI, the dissolution of the brown solid was slow. The electronic spectra of the brown solids in MeCN contain a band at 330 nm (λ_{max}) which indicated that I_3^- is present.

The reactions of NaI and KI with WF_6 in CH_2Cl_2 show behaviour similar to that of NaI and KI with MoF_6 in CH_2Cl_2. However, the reactions are extremely slow. The electronic spectra indicated that some I_2 was released in the reaction and that I_3^- was produced on the surface of the solid iodides.

3-2-3 Comparisons Among the Reactions.

The solubility of ionic iodides is crucial for the syntheses to be satisfactory. Tetra-n-butylammonium iodide is soluble in both CH_2Cl_2 and SO_2. This is an important factor so that Bu_4NI readily reduces MoF_6 and WF_6 in CH_2Cl_2 and SO_2 (equation 3-4)

$$2Bu_4NI + 2MF_6 \xrightarrow{CH_2Cl_2 \text{ or } SO_2} 2Bu_4NMF_6 + I_2 \qquad (3\text{-}4)$$

(M = Mo, W)

It was observed that the reactions involving MoF_6 appear to be more rapid than those involving WF_6. This phenomenon is seen very clearly in the reactions of alkali-metal iodides and MoF_6 and WF_6 in these two solvents.

The electrochemical behaviour of MoF_6^- salts and iodides are reported in Chapter Four. The comparison of the half-wave potentials of MoF_6/MoF_6^- and WF_6/WF_6^- couples with those of the iodide couples of Bu_4NI shows that the iodide, Bu_4NI is expected to reduce MoF_6 or WF_6 easily to MoF_6^- or WF_6^- in MeCN or CH_2Cl_2.

Sodium iodide and potassium iodide readily reduce MoF_6 or WF_6 in SO_2 at -60^oC (equation 3-5)

$$2AI + 2MF_6 \xrightarrow{SO_2} 2AMF_6 + I_2 \qquad (3\text{-}5)$$

(A = Na, K) (M = Mo, W)

This is in agreement with previous work.[41] The reaction involving WF_6 is relatively slower than that of MoF_6.

The reactions of NaI and KI with MoF_6 or WF_6 in CH_2Cl_2 are very slow and incomplete at room temperature. As mentioned above this is likely to be due to the insolubility of NaI and KI. The surface of the solids appear to react firstly with MoF_6 or WF_6 presumably according to equation 3-6,

$$2AI + 2MF_6 \xrightarrow{CH_2Cl_2} 2AMF_6 + I_2 \qquad (3\text{-}6)$$

(A = Na, K) (M = Mo, W)

and then I_2, which is produced, reacts with solid NaI or KI to give the I_3^- anion. The reaction involving MoF_6 appears to be much faster than that involving WF_6.

Dichloromethane is a non-polar and aprotic solvent, because of these properties and its low dieletric constant, its ionizing capability towards many ionic compounds is very low. Therefore,

the solubilities of many ionic compounds such as NaI and KI, whose lattice energies are relatively large, are very limited. On the other hand, the effect of liquid SO_2 is different. Because SO_2 has a relatively higher dielectric constant, compared to CH_2Cl_2, at reaction temperature (22.3 at -60°C), its ionizing ability towards ionic compounds at -60°C should be higher than that of CH_2Cl_2 at 20°C. The alkali metal iodides such as NaI and KI are reasonably soluble in this solvent and I^- anion is better solvated by SO_2 than it is in CH_2Cl_2.

The reactions involving KI are somewhat slower than those of NaI in each solvent and with each oxidizing agent. This observation may be due to the slower dissolution of KI in these solvents compared to that of NaI. The reactions of the iodides with the hexafluorides, MoF_6 and WF_6 in CH_2Cl_2 and SO_2 are summarized in Table 3-6. The qualitative order of the rates of the reactions observed appears to be as follows:

$Bu_4NI + MoF_6$ (in SO_2), $NaI + MoF_6$ (in SO_2) > $KI + MoF_6$ (in SO_2) > $Bu_4NI + WF_6$ (in SO_2), $NaI + WF_6$ (in SO_2) > $KI + WF_6$ (in SO_2) > $Bu_4NI + MoF_6$ (in CH_2Cl_2) > $Bu_4NI + WF_6$ (in CH_2Cl_2) > $NaI + MoF_6$ (in CH_2Cl_2) > $KI + MoF_6$ (in CH_2Cl_2) > $NaI + WF_6$ (in CH_2Cl_2) > $KI + WF_6$ (in CH_2Cl_2).

It seems that the most important feature affecting the rate is the nature of the solvent, secondly, although there is an exception for the reaction involving Bu_4NI, the difference in the oxidizing power of the hexafluorides, and thirdly the nature of the iodides.

Table 3-6 The Reactions of Bu_4NI, NaI and KI with the hexafluorides, MoF_6 and WF_6, in CH_2Cl_2 and liquid SO_2.

Reducer / solvents / oxidiser / results.	SO_2		CH_2Cl_2	
	MoF_6	WF_6	MoF_6	WF_6
Bu_4NI	Bu_4NMoF_6, I_2 very fast At -60°C	Bu_4NWF_6, I_2 fast At -60°C	Bu_4NMoF_6, I_2 fast Room temp.	Bu_4NWF_6, I_2 fast Room temp.
NaI	41 $NaMoF_6$, I_2 very fast At -60°C	41 $NaWF_6$, I_2 fast At -60°C	$NaMoF_6$, I_2 incomplete slow room temp.	$NaWF_6$, I_2 incomplete very slow room temp.
KI	41 $KMoF_6$, I_2 very fast At -60°C	41 KWF_6, I_2 fast At -60°C	$KMoF_6$, I_2 incomplete slow room temp.	KWF_6, I_2 incomplete very slow room temp.

3-2-4 Reaction of Copper(I) hexafluorometallate(V) Salts with Bu_4NI in CH_2Cl_2.

The salts $[Cu(MeCN)_4][MoF_6]$ and $[Cu(MeCN)_4][WF_6]$ were quite soluble in CH_2Cl_2.

The reaction of $[Cu(MeCN)_4][MoF_6]$ and Bu_4NI in CH_2Cl_2 at room temperature produced a finely divided dun colour solid, which precipitated from the solution immediately after the two reactants were mixed. The electronic spectrum of the solution showed no band which was due to I_2, so I_2 was not produced in the reaction. A very pale yellow soluble product was isolated from the solution. This product is very sensitive to moisture and immediately became blue when it was exposed to the atmosphere. The infrared spectrum for the solid state of the soluble product contained two strong bands at 635 cm^{-1} and 250 cm^{-1}. These should be assigned to the ν_3 and ν_4 vibrations of the hexafluoromolybdate(V) ion respectively. The ν_3 and ν_4 vibrations of the hexafluoromolybdate(IV) are at 540 cm^{-1} and 255 cm^{-1} respectively,[43] but there were no absorption bands observed at these positions in the spectrum. Thus hexafluoromolybdate(IV) did not appear to be produced in this reaction. The i.r. spectrum of the soluble product also showed the bands which were due to the presence of the Bu_4N^+ cation. There was no absorption band at 2300 cm^{-1} region in this spectrum, therefore, MeCN was not present in this product. The spectral data are listed in Table 3-7. According to the spectroscopic study and the determination of the stoichiometry of this reaction, which was 1:1, the interaction appears to lead to a reaction according to equation 3-7

$$[Cu(MeCN)_4][MF_6] + Bu_4NI \xrightarrow{CH_2Cl_2} CuI + Bu_4NMF_6 + 4MeCN \qquad (3\text{-}7)$$

(M = Mo, W)

The observations of the reaction of $[Cu(MeCN)_4][WF_6]$ and Bu_4NI in CH_2Cl_2 were the same as described above. No further reduction of WF_6^- was observed in the spectroscopic study, and the stoichiometry determination indicated a 1:1 ratio. The resulting reaction appears to be the reaction described in equation 3-7. The infrared spectrum of the soluble pale yellow solid contained two strong bands at 595 cm^{-1} and 238 cm^{-1}, which were due to the vibrational modes ν_3 and ν_4 respectively for the WF_6^- anion, and also contained bands which attributed to the presence of the Bu_4N^+ cation (Table 3-7). The electronic spectrum for the solution of the soluble product confirmed that no I_2 was produced in the reaction.

3-2-5 Reactions Between Bu_4NMoF_6 and Bu_4NI in CH_2Cl_2 and SO_2.

The interaction between Bu_4NI and Bu_4NMoF_6 was investigated using CH_2Cl_2 as solvent. According to the infrared spectrum, which contained only bands at 635 cm^{-1} and 250 cm^{-1} due to MoF_6^- and bands for Bu_4N^+ cation (Table 3-8), and electronic spectrum, which indicated that no I_2 was released, no reaction occurred. Neither did any reaction occur between Bu_4NI and Bu_4NMoF_6 in SO_2 at -60^oC. The infrared spectrum of the soluble solid isolated from the mixture is listed in Table 3-8 and is identical to that of Bu_4NMoF_6.

Table 3-7 Infrared Spectra of the soluble products from the reactions of $[Cu(MeCN)_4][MoF_6]$ and $[Cu(MeCN)_4][WF_6]$ with Bu_4NI in CH_2Cl_2.

$[Cu(MeCN)_4][MoF_6]$ + Bu_4NI ν_{max} (cm^{-1})	$[Cu(MeCN)_4][WF_6]$ + Bu_4NI ν_{max} (cm^{-1})	Assignment
1033 m	1033 m	$(C_4H_9)_4N^+$ band
930 m	930 m	" "
881 m	883 m	" "
739 m	740 m	" "
630 s		ν_3 (MoF_6^-)
	595 s	ν_3 (WF_6^-)
250 s		ν_4 (MoF_6^-)
	238 s	ν_4 (WF_6^-)

s = strong, m = medium

Table 3-8 Infrared spectra of the soluble solid from the Bu_4NMoF_6 + Bu_4NI in CH_2Cl_2 and liquid SO_2.

In CH_2Cl_2 ν_{max} (cm^{-1})	In SO_2 ν_{max} (cm^{-1})	Assignment
1030 m	1031 m	$(C_4H_9)_4N^+$ band
924 m	924 m	" "
882 m	882 m	" "
738 m	738 m	" "
635 s	635 s	ν_3 (MoF_6^-)
250 s	250 s	ν_4 (MoF_6^-)

s = strong, m = medium

3-2-6 Reactions of MoF_6^- Salts with Ionic Iodides in Liquid SO_2.

A mixture of $NaMoF_6$ and Na_2MoF_6 salts was obtained from the equimolar reaction of NaI and $NaMoF_6$ in SO_2 at -60°C. The solid state infrared spectrum contained bands at 635 and 250 cm^{-1} which were due to the vibrations ν_3 and ν_4 respectively for MoF_6^-, and 540 and 255 cm^{-1} which were for ν_3 and ν_4 vibrations respectively for MoF_6^{2-}. The data of the spectrum are listed in Table 3-9. In the infrared spectrum, which contained the bands due to both MoF_6^- and MoF_6^{2-}, it can be seen that the isolated product was a mixture of hexafluoromolybdate(V) and (IV).

The frequencies for the ν_4 vibrations of MoF_6^- and MoF_6^{2-} are very close together, so the band for MoF_6^{2-} (255 cm^{-1}) appeared as a shoulder to the high frequency side of the ν_4 vibration of MoF_6^-. The assignment of the bands due to MoF_6^{2-} was made by comparison with the data of the infrared spectrum of the caesium salt.[43] The ν_3 mode frequency is significantly smaller for MoF_6^{2-} salt compared with that for MoF_6 (741 cm^{-1})[85] and MoF_6^- (635 cm^{-1}).[84] The decrease in frequency through the series is in line with the increase in the Mo-F distance with decreasing oxidation state for molybdenum and with increasing overall negative charge.[43]

The I_2 released from the reaction of $NaMoF_6$ and NaI was weighed and it corresponded to about 57% reduction of $NaMoF_6$ to Na_2MoF_6.

Table 3-9 Infrared spectrum of the product of the reaction of equi-molar NaI and $NaMoF_6$ in SO_2.

Frequencies $\nu_{max}(cm^{-1})$	Assignments
635 s	ν_3 (MoF_6^-)
540 s	ν_3 (MoF_6^{2-})
255 sh	ν_4 (MoF_6^{2-})
250 s	ν_4 (MoF_6^-)

s = strong, sh = shoulder

3-2-7 Comparisons Among the Reactions.

Although sodium iodide can reduce $NaMoF_6$ to Na_2MoF_6 in sulphur dioxide, the hexafluoromolybdate(V) salts were not reduced by Bu_4NI in CH_2Cl_2. This phenomenon is consistent with the results obtained in the electrochemical study of these compounds. The electrochemical properties will be discussed in Chapter Four. It is not surprising that hexafluorotungstate(V) salts were not reduced by Bu_4NI, since the oxidizing ability of hexafluorotungstate(V) salts is much lower than that of hexafluoromolybdate(V) salts.[8]

The chemistry of copper complexes has been studied extensively. The most common oxidation states of copper are (I) and (II). In aqueous solution Cu(I) ion is unstable with respect to disproportionation to Cu^{2+} and Cu (equation 1-1), but the copper(I) ion is better solvated and stabilized by acetonitrile than by water.[87] This presumably is due to the Cu(I) ion having a filled d^{10} outer electron shell, which undergoes a specific $d\pi - p\pi$ interaction with the π^* orbital of the nitrile group. The potential of the couple, solvated Cu^{II}/solvated Cu^{I}, determined by cyclic voltammetry using $[Cu^{II}(MeCN)_6][PF_6]_2$ and $[Cu^{I}(MeCN)_4][PF_6]$ in MeCN have been reported to be 0.71 and 0.75V vs. Ag^+/Ag respectively.[88] The slight difference in the half wave potential for the Cu(II) and Cu(I) salts probably reflects the difference in coordination numbers. From the present study of the salts $[Cu(MeCN)_4][MoF_6]$ and $[Cu(MeCN)_4][WF_6]$ it can be seen that the coordinated MeCN was removed from the Cu^{I} central ion in the reaction of these salts with Bu_4NI in CH_2Cl_2. The Cu^{I} cation immediately interacts with I^- to precipitate from

the solution as CuI suggesting that CuI is formed easier than the solvated salts $[Cu(MeCN)_4][MoF_6]$ and $[Cu(MeCN)_4][WF_6]$ in CH_2Cl_2 solution. The spectroscopic study and the stoichiometry determination showed that solvated hexafluoromolybdate(IV) was not produced in CH_2Cl_2 solution. The reducing ability of the iodide Bu_4NI used was not strong enough to reduce hexafluoromolybdate(V) salts to hexafluoromolybdate(IV) salts even though all species were soluble.

3-2-8 Magnetic Measurements of some Hexafluoromolybdate(V) Salts.

The magnetic properties of several MoF_6^- salts have been reported by Hargreaves and Peacock over a wide range of temperatures.[42] Since their work was carried out before the possibility of reducing MoF_6^- to MoF_6^{2-} was recognised[43] a reinvestigation was thought desirable using MoF_6^- salts prepared via routes in which the presence of MoF_6^{2-} could reasonably be excluded.

Three samples (I) $NaMoF_6$ (from NaI + MoF_6 in SO_2), (II) Bu_4NMoF_6 (from Bu_4NI + MoF_6 in CH_2Cl_2) and (III) Bu_4NMoF_6 (from $[Cu(MeCN)_4][MoF_6]$ + Bu_4NI in CH_2Cl_2) were investigated and variable temperature magnetic moment measurements were carried out by Dr. Peter Thornton (Department of Chemistry, Queen Mary College, University of London) over the temperature range 80 - 300 K (Table 3-10). The moments obtained for these complexes do not follow the simple Curie Law (equation 3-8),

$$\chi_m^{corr} = C/T \qquad (3\text{-}8)$$

where C is the Curie constant, χ_m^{corr} is the corrected molar

Table 3-10 Magnetic Moments of Mo(V) in Na^+ and Bu_4N^+ hexafluoromolybdates(V) salts over temperature range given below.

(I) $NaMoF_6$		(II) Bu_4NMoF_6		(III) Bu_4NMoF_6	
Temperature (K)	$\mu_{\mu B}$	Temperature (K)	$\mu_{\mu B}$	Temperature (K)	$\mu_{\mu B}$
79.0	1.10	95.8	1.47	108.9	1.10
99.1	1.21	116.1	1.45	125.0	1.28
119.4	1.27	136.7	1.53	144.9	1.26
138.6	1.34	156.5	1.61	163.7	1.26
156.5	1.39	175.2	1.67	183.3	1.37
178.8	1.45	197.4	1.69	204.4	1.43
219.0	1.57	217.2	1.76	223.0	1.35
237.7	1.60	236.2	1.79	243.8	1.41
257.0	1.61	254.9	1.82	263.9	1.40
278.9	1.65	275.8	1.84	283.9	1.42
298.1	1.69	297.8	1.86	298.5	1.43
Error in $\mu \pm 4\%$		Error in $\mu \pm 4\%$		Error in $\mu \pm 7\%$	

susceptibility, and T is the absolute temperature. However it is interesting to notice that all the plots (Fig. 3-1) of $^{1}/\chi_m^{corr}$ against absolute temperature T fit the Curie-Weiss relationship (equation 3-9)

$$\chi_m^{corr} = C/(T-\theta) \qquad (3\text{-}9)$$

where θ is the temperature at which the line cuts the T axis, and is known as the Weiss constant.

The plot of the experimental change of μ_{eff} with T is shown in Fig. 3-2. A comparison with Hargreaves and Peacock's plot[42] of this kind is also shown in Fig. 3-2. Although the magnitudes of the values are different, the experimental change of the values with temperature is very similar. The values obtained previously are somewhat lower than the values obtained in the present work. Iqbal measured room temperature magnetic moments of Mo(V) in Ag(I) and Ag(III) complexes and obtained even lower values[62] (1.00 $\pm$ 0.06 and 0.93 $\pm$ 0.08 B.M.). The values obtained in the present work approach the spin-only value for a d^1 configuration.

The spin-only value for a d^1 configuration is μ = 1.73 B.M. In the first transition series, the magnetic moment is frequently close to the spin-only value corresponding to the number of unpaired electrons involved, and deviation from this figure is mostly towards higher values. This is because the orbital motion of the electrons also makes a contribution to the moment. Therefore, the simple idea of the magnetic behaviour of the d-block elements, which relates paramagnetism directly to the number of unpaired spin electrons is especially useful for the first

transition series, but it has less value when applied to the second and third rows. More complex behaviour is often encountered in compounds of these heavier elements. The magnetic moments for these elements differ considerably from the spin-only values and often markedly with temperature. Spin-orbital coupling can lower the measured value of the magnetic susceptibilities of these heavier elements from those of the spin-only values. Therefore a lower value of the magnetic susceptibility for Mo^{V} is expected. However, the spin-free d^{1} (t_{2g}) configuration for this ion (Mo^{V}) should retain some orbital contribution to the magnetic moment in octahedral complexes. This effect will make the measured value higher.

The values for all three samples show (Table 3-10) that the moments are highly temperature dependent. When the temperature increases, the values increase markedly. For the three samples, the values of the moment are the highest for Bu_4NMoF_6 (sample II) and are the lowest for Bu_4NMoF_6 (sample III). Values for $NaMoF_6$ are lower compared with those of Bu_4NMoF_6 (sample II). The higher values could have been caused by the orbital contribution which is caused by the d^{1} electron motion in three t_{2g} orbitals. The orbital contribution in Bu_4NMoF_6 appears to be stronger than that in $NaMoF_6$. This could be a result of the different cations in these compounds. The electric fields of other atoms, ions and molecules surrounding the metal ion Mo^{V} in its compounds restrict the orbital motion of the electrons so that the orbital angular momentum, hence the orbital moments, are wholly or partially quenched. The cation Na^{+} is much smaller compared with the

Bu_4N^+ cation, therefore the ability of penetration of Na^+ to the Mo^V ion through the ligands is much larger than that of Bu_4N^+. As a result, the electric field of Na^+ ion could influence the Mo^V ion in the complex, and restrict the orbital motion of d^1 electron more strongly. This effect makes the orbital contribution lower. In the Bu_4NMoF_6 case, this effect appears to be very small.

The observed magnetic moment for Bu_4NMoF_6 (sample III) is markedly lower compared to that of Bu_4NMoF_6 (sample II). The sample (III) is prepared by the reaction of $[Cu(MeCN)_4][MoF_6]$ with Bu_4NI in CH_2Cl_2 (see experimental section of this chapter). In this preparation, the separation of soluble product (III) Bu_4NMoF_6 was very difficult, and there could be some unreacted Cu^+ and Bu_4NI present. This impurity may result in a lower value of μ_{eff} compared to that for (II) Bu_4NMoF_6, which was prepared directly from the reduction of MoF_6 using Bu_4NI in CH_2Cl_2 where excess of MoF_6 was easily removed from the product by pumping in the vacuum line.

The magnetic moment values obtained in the present work are quite high compared to the values obtained in Iqbal's work. The higher magnetic moments may be due to the presence of small quantities of MoF_6^{2-} in the product. Although there was no evidence for the presence of MoF_6^{2-} in the solids from their infrared spectra, the technique of magnetic moment measurement is probably more sensitive to the presence of trace impurities. Further magnetic measurements will be required to provide a definitive explanation for the behaviour observed.

Figure 3-1 Plots of $1/\chi_m$ against temperature (K)

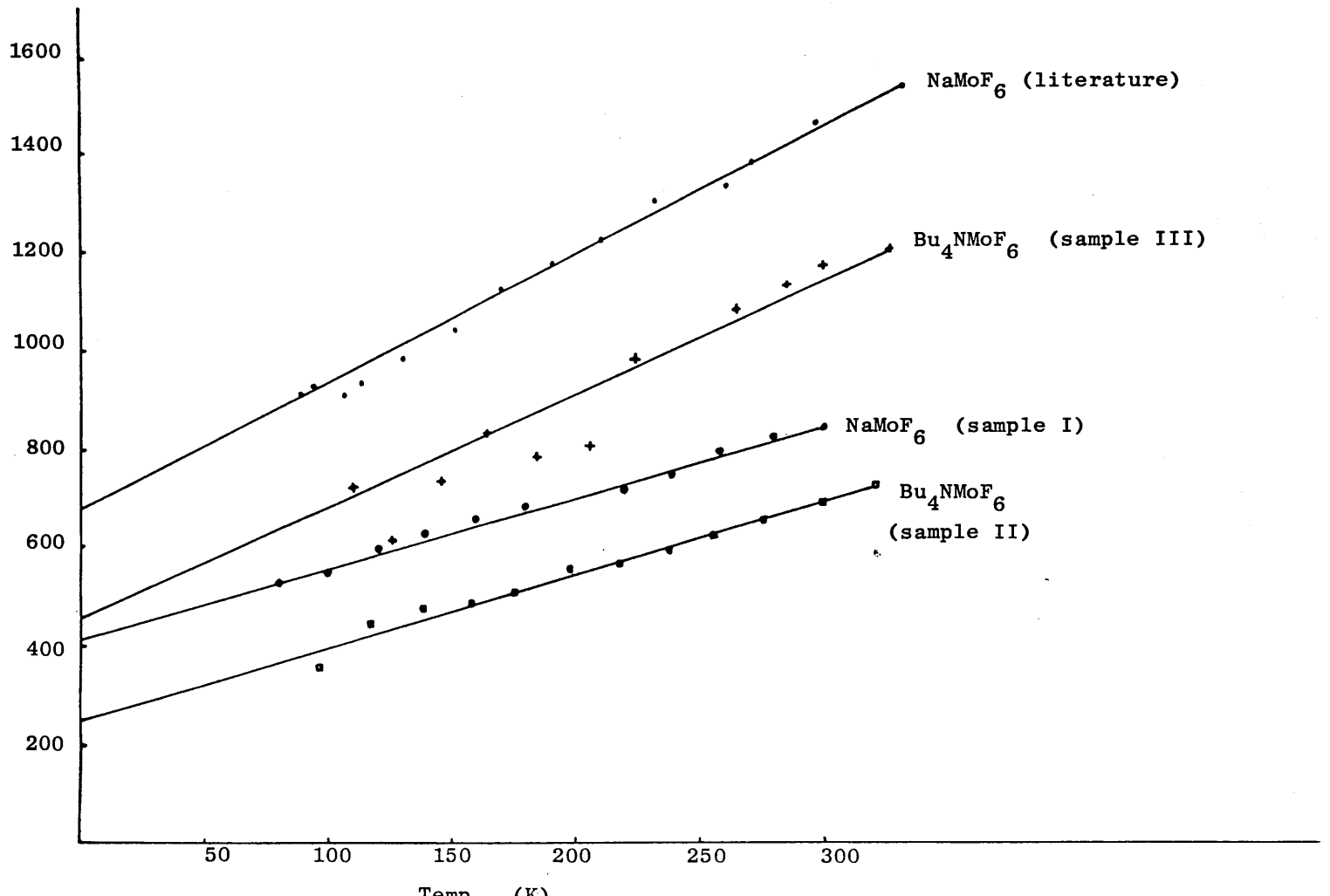
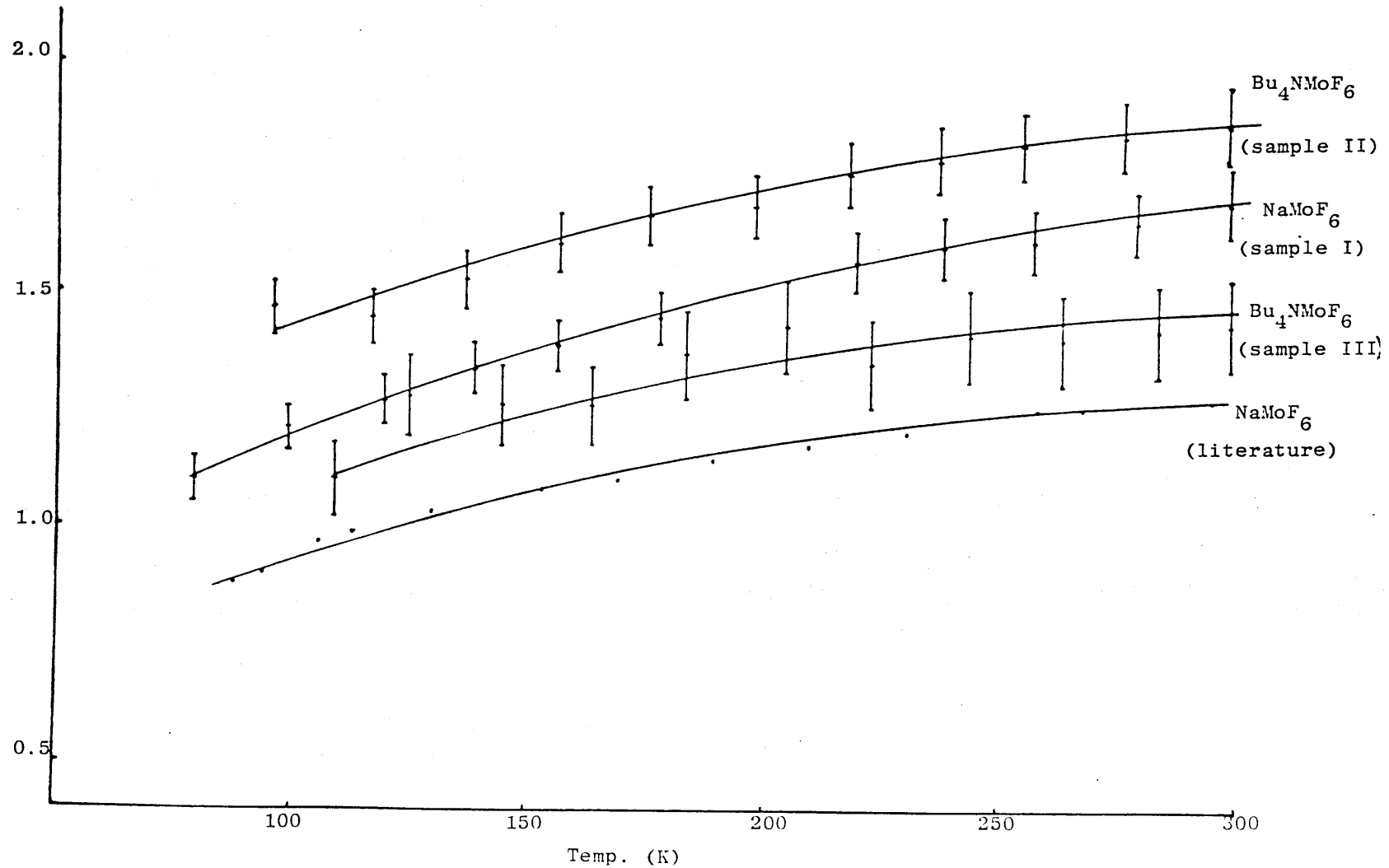


Figure 3-2 Plots of μ_{eff} against temperature (K)



3-3 Conclusion

Solvents have significant effects on the redox reaction of iodides with the hexafluorides of Mo and W. Dichloromethane is not an appropriate solvent for the reactions involving NaI and KI because of the insolubility of these ionic inorganic compounds. Molybdenum and tungsten hexafluorides are readily reduced to Mo^{V} and W^{V} salts by Bu_4NI both in CH_2Cl_2 and SO_2. However, further reduction of MoF_6^- and WF_6^- is difficult in these reactions, although mixtures of MoF_6^- and MoF_6^{2-} salts were obtained in the reaction of MoF_6 and excess of alkali metal iodides in SO_2.

3-4 Experimental

All the manipulations, loading of chemicals in the reaction vessels, handling of reagents and the preparation of samples for spectroscopic analysis, described throughout the work, were carried out by using a conventional high vacuum system and an oxygen free nitrogen atmosphere glove box. The high oxidation state fluorides, MoF_6 and WF_6 were prepared as described in Chapter Two and purified by low temperature trap-to-trap distillation over activated NaF in break-seal vessels at $-196^{o}C$. Solid Bu_4NI (Aldrich Chemical Co Ltd), NaI (Riedel-De Haen Ag Seelze-Hannover), and KI (May and Baker) were dried by pumping. Solid chemicals were weighed in the glove box using an electronic balance (Sartorius H120).

3-4-1 Preparation of Bu_4NMF_6 (M=Mo,W) in CH_2Cl_2.

A double limb vessel was evacuated on the vacuum line and flamed out with a gas-oxygen torch. The vessel was loaded with Bu_4NI (0.5 mmol) in the glove box, and re-attached to the vacuum line and re-evacuated. Dichloromethane (5 cm^3) and MoF_6 were added by vacuum distillation at -196°C using liquid nitrogen. On warming to room temperature, a dark pink solution was obtained. The solution was decanted into the empty limb of the vessel and the volatile materials (I_2, CH_2Cl_2 and excess MoF_6) were removed by vacuum distillation. To avoid bumping the solution was held at about -70°C and then the temperature was raised as the distillation proceeded. Dark grey solids were isolated at first. To wash away the I_2 from the product, more CH_2Cl_2 was added and removed together with I_2. After washing several times a pale yellow solid product was obtained. The i.r. spectrum of the product had bands at ν_{max} 635 cm^{-1} and 250 cm^{-1} which were assigned to MoF_6^- and the electronic spectrum of the pink solution contained a band at λ_{max} 505 nm which was due to I_2.

The preparation of Bu_4NWF_6 was identical to that of Bu_4NMoF_6. The infrared spectrum of the product contained bands at ν_{max} 600 cm^{-1} and 240 cm^{-1} which were assigned to WF_6^- anion, and electronic spectrum of the pink solution contained a band at λ_{max} 505 nm (I_2 transition).

3-4-2 Reactions of NaI and KI with MoF_6 and WF_6 in CH_2Cl_2.

The procedure for these reactions was very similar to that used in the preparation of Bu_4NMoF_6. An evacuated and flamed out double limb vessel was transferred to the glove box, and loaded with NaI (1 mmol) or KI (1 mmol). The vessel was re-evacuated on the vacuum line, and CH_2Cl_2 (5 cm^3) was added. The iodides were not soluble. An excess of MoF_6 was distilled into the reaction vessel. In both cases, when the reaction mixture was allowed to warm to room temperature, the colour of the solution and the solid was yellow. After the mixture was shaken for about two hours, in the case of NaI, longer in the case of KI, the liquid became pink and the solid became brown.

In the WF_6 case, the materials were mixed in a similar manner. In the mixture of NaI, CH_2Cl_2 and WF_6, the colour of the solution and the solid was pale yellow when it was allowed to warm to room temperature. After it was shaken overnight, the solution became pink and the solid became brown. The mixture of KI, CH_2Cl_2 and WF_6 was colourless when it was warmed to room temperature. After it was shaken for a longer time, the solution phase became pale pink and the solid became pale brown. In all these reactions, insufficient products were obtained for i.r. examination. The electronic spectrum of the pink solution contained a band at λ_{max} 505 nm (I_2 transition).

3-4-3 Preparation of Bu_4NMF_6, $NaMF_6$ and KMF_6 (M=Mo,W) in SO_2.

The ionic iodides (0.5 ~ 1.0 mmol) were loaded in flamed out double limb vessels in the glove box. Sulphur dioxide (5 cm^3) and excess of the hexafluorides were added by vacuum distillation. During the distillation of SO_2, the solvent was held at about -60°C, and collected in the reaction vessel at -196°C. When the mixture was warmed to -60°C, the SO_2 liquified and iodine was released from the reaction. The I_2 together with SO_2 were removed. Further SO_2 was added and removed several times to wash the solute. Colourless crystalline products were obtained and pumped for a while on the vacuum line to remove all volatile material. Infrared spectra of the products showed bands due to hexafluoro-metallate(V) anions.

3-4-4 Preparation of $[Cu(MeCN)_4][MF_6]$ (M= Mo, W)

Excess of Cu metal was loaded in a flamed out double limb vessel in the glove box. MeCN (10 cm^3) and MoF_6 or WF_6 was distilled at -196°C. On warming to room temperature a green (pale green for the WF_6 case) solution was obtained which became yellow after overnight shaking at room temperature. From this solution yellow solid was isolated after removal of the volatile material. This yellow product was characterised to be $[Cu(MeCN)_4][MF_6]$ by its i.r. spectrum.[5]

3-4-5 Reaction of $[Cu(MeCN)_4][MF_6]$ (M=Mo, W) with Bu_4NI in CH_2Cl_2

A frangible ampoule was joined to a Rotaflo or J. Young stop-cock, then evacuated and flamed out. The ampoule was loaded with a weighed quantity of $[Cu(MeCN)_4][MF_6]$ and vacuum sealed.

The ampoule was placed into a flamed out double limb vessel and a weighed quantity of Bu_4NI to give a mole ratio of 1:1 versus $[Cu(MeCN)_4][MF_6]$, was added to the vessel in the glove box. Solvent CH_2Cl_2 (10 cm^3) was vacuum distilled into the vessel. The reaction mixture was allowed to warm to room temperature so that Bu_4NI dissolved. The double limb vessel was shaken and the frangible ampoule broken. As a result the reactants Bu_4NI and $[Cu(MeCN)_4][MF_6]$ were mixed.

Immediately after the two reactants were mixed, a finely divided dun colour solid precipitated from the solution. After the precipitate had settled down completely (this required several hours) the solution was decanted into the empty limb. The solvent was removed from the soluble product. The infrared spectrum of the product showed the characteristic bands of MF_6^- anions. The stiochiometry data are listed in Table 3-11 and Table 3-12.

3-4-6 Preparation of Na_2MoF_6 in SO_2.[43]

A weighed quantity of NaI was treated with excess of MoF_6 in SO_2 solution to produce $NaMoF_6$ in double limb vessel with the procedure similar to that described in the previous sections. The SO_2, excess of MoF_6, and iodine were removed by pumping in vacuo. A second quantity of NaI, equal to the first, was added to the solid product $NaMoF_6$ in the glove box, and more SO_2 was added on the vacuum line. Iodine was released in the sulphur dioxide solution. The I_2 and SO_2 were removed accompanied by gradually warming to room temperature and collected in another vessel. Further quantities of SO_2 were added and the procedure was repeated until virtually no iodine was released. This was carried out by

Table 3-11 The Stoichiometry of the reaction $[Cu(MeCN)_4][MoF_6]$ + $Bu_4NI \rightarrow CuI + Bu_4NMoF_6 + 4MeCN$

Number of Reaction		$[Cu(MeCN)_4][MoF_6]$	Bu_4NI	CuI	Bu_4NMoF_6
1	Wt(g)	0.11	0.093	0.050	0.082
	mmol	0.25	0.25	0.26	0.18
2	Wt(g)	0.438	0.370	0.179	0.373
	mmol	1.00	1.00	0.94	0.82
3	Wt(g)	1.184	0.999	0.391	1.10
	mmol	2.7	2.7	2.05	2.43

Table 3-12 The Stoichiometry of the reaction $[Cu(MeCN)_4][WF_6]$ + $Bu_4NI \rightarrow CuI + Bu_4NWF_6 + 4MeCN$

Number of Reaction		$[Cu(MeCN)_4][WF_6]$	Bu_4NI	CuI	Bu_4NWF_6
1	Wt(g)	0.132	0.093	0.051	0.118
	mmol	0.25	0.25	0.27	0.22
2	Wt(g)	0.263	0.185	0.0936	0.197
	mmol	0.50	0.50	0.49	0.37
3	Wt(g)	0.526	0.370	0.174	0.374
	mmol	1.00	1.00	0.91	0.69

five additions of the solvent. All the iodine for this second step was collected, and separated from the SO_2 by holding the vessel at -80°C to remove SO_2 by vacuum distillation to a -196°C vessel. The iodine was weighed on an analytical balance. The infrared spectrum showed that the product was a mixture of $NaMoF_6$ and Na_2MoF_6.

CHAPTER FOUR

A STUDY BY CYCLIC VOLTAMMETRY OF HEXAFLUOROMOLYBDATE(V) AND SOME IONIC IODIDES IN DIFFERENT SOLVENTS.

4-1 INTRODUCTION

4-1-1 Cyclic Voltammetry of Hexafluoromolybdate(V).

The redox couples MoF_6/MoF_6^- and WF_6/WF_6^- have been determined in anhydrous hydrogen fluoride[45,46] and in acetonitrile[58,89,90] using cyclic voltammetry. The half-wave potentials of the MoF_6/MoF_6^- and WF_6/WF_6^- couples in anhydrous HF are 0.91V and -0.10V vs. Cu/CuF_2 respectively.[45,46] Heath et al studied the electrochemical properties of alkali metal hexafluorotungstates(V) in MeCN using cyclic voltammetry and found $E_{\frac{1}{2}}(WF_6/WF_6^-)$ = 0.81V vs. SCE. They established that the hexafluorotungstate(V) ion does not undergo reduction in acetonitrile at a platinum electrode over a wide cathodic range.[89] The electrochemical processes $[MF_6]^{n-} \rightleftharpoons [MF_6]^{-(n+1)}$ (M = Nb, Mo, Tc, Ru, Ta, W, Re and Os) have been studied by cyclic voltammetry and polarography in MeCN for a series of transition metals. The observed potentials show a correspondence with the number of d electrons and emphasise the expected greater oxidizing power of second-row elements over the third row elements. The half-wave potentials were found to be +1.70, -0.35 and -2.25V vs. Ag^+/Ag for the couples Mo^{VI}/Mo^V, Mo^V/Mo^{IV}, and Mo^{IV}/Mo^{III} respectively and + 0.70, -1.30 and < -3.0V vs. Ag^+/Ag for the couples W^{VI}/W^V, W^V/W^{IV} and W^{IV}/W^{III} respectively.[50,90]

The redox behaviour of molybdenum hexafluoride in acetonitrile at 25°C has been compared with other redox couples using cyclic voltammetry and appropriate redox reactions under carefully controlled conditions.[8] The order of oxidizing ability is established as follows: $UF_6 > MoF_6 > NO^+ >$ solvated $Cu^{2+} \geq WF_6$. Anderson et al found the half-wave potentials + 1.60, and -0.35V

vs. Ag^+/Ag for MoF_6/MoF_6^- and MoF_6^-/Mo^{IV} respectively and + 0.51 and -1.50 V vs. Ag^+/Ag for WF_6/WF_6^- and WF_6^-/W^{IV} respectively in the study of redox properties of $Cu(MoF_6)4MeCN$ and $Cu(WF_6)4MeCN$ in MeCN using cyclic voltammetry.[8]

The cyclic voltammogram of $[I(NCMe)_2][MoF_6]$ in MeCN contains a quasi-reversible wave, $E_{\frac{1}{2}}$ = 1.60V vs. Ag^+/Ag, due to the MoF_6/MoF_6^- couple.[83]

All the work described above has resulted in very similar values for the half-wave potentials of the couples, MoF_6/MoF_6^- and MoF_6^-/Mo^{IV} in MeCN.

The compound $NOPF_6$ has been studied using cyclic voltammetry and gives rise to a quasi-reversible wave due to the couple NO^+/NO. The half-wave potential has been found to be $E_{\frac{1}{2}}$ = 0.87V vs. Ag^+/Ag and the peak to peak separation is ΔEp = 0.27V.[8] It is proposed that the lack of complete reversibility of the wave of NO^+/NO couple may be due to the solvation of NO^+ in MeCN, and this effect may change the geometry between the oxidized and reduced forms.[8] The effective solvation of NO^+ by MeCN has been suggested from the shift of the NO^+ stretching frequency; the stretching frequency of NO^+ in MeCN is 1865 cm^{-1}, but that in solid $NOPF_6$ is 2340 cm^{-1}.[39]

4-1-2 Cyclic Voltammetry of Ionic Iodides.

The cyclic voltammograms of iodides in acetonitrile consist of two waves,[91] which have been assigned to the I_3^-/I^- and I_2/I_3^- couples.

$$3I^- \longrightarrow I_3^- + 2e^- \qquad (4\text{-}1)$$

$$2I_3^- \longrightarrow 3I_2 + 2e^- \qquad (4\text{-}2)$$

The reduction potential of I_3^- appears to be more negative than that of I_2. This is consistent with the stabilization of I_2 by complexation with I^-. The wave of the I_3^-/I^- couple is distorted and appears to be irreversible.[91] It has been proposed that the iodide ion or iodine could be adsorbed onto the platinum electrode and that this adsorbed layer is not electroactive. Anderson studied the cyclic voltammetry of some compounds containing iodine and obtained the half-wave potentials of 0.310 and -0.150V vs. Ag^+/Ag for Bu_4NI and 0.300 and -0.200V vs. Ag^+/Ag for LiI due to the couples I_2/I_3^- and I_3^-/I^- respectively.[91]

Recently, the electrochemical behaviour of iodide was studied in propylene carbonate using cyclic voltammetry. In an anodic sweep, iodide is oxidized sequentially to triiodide and then to iodine. This mechanism was confirmed using UV-visible spectroscopy in conjunction with cyclic voltammetry experiments at a thin gold mesh electrode.[92] The reaction 4-1 is sluggish in comparison to reaction 4-2.

Cyclic voltammetric experiments on Bu_4NI at a platinum electrode in propylene carbonate and in propylene carbonate containing increasing amounts of SO_2 were carried out by Koval and Drew.[93] In the absence of SO_2, the I_3^-/I^- and I_2/I_3^- couples occur as an irreversible wave and a quasi-reversible wave, with peak to peak separations of 0.41 and 0.091V, respectively. An anodic shift in peak potentials for the I_3^-/I^- couple occurs when the concentration of SO_2 increases in the solution. This suggests that SO_2 has a catalytic effect on the electrode kinetics of the I_3^-/I^- couple. However, the potential of the I_2/I_3^- couple is reported to remain

constant within experimental error.

4-1-3 Electrochemistry in Liquid Sulphur Dioxide.

Garcia et al have reported that the anodic potential range of sulphur dioxide for use in electrochemical studies can be extended to about +4.0V versus a silver quasi-reference electrode using tetra-n-butylammonium hexafluoroarsenate as supporting electrolyte. The cathodic limit is reported to be -0.7V versus the same reference electrode.[94] This wide range, extending to very positive potential makes liquid SO_2 particularly useful for studying electrochemical oxidations. The electrochemical reaction which limits the cathodic potential range for this solvent is believed to be the reduction of SO_2 itself:

$$SO_2 + e^- \rightleftharpoons SO_2^{\cdot -} \qquad (4\text{-}3)$$

The limiting anodic electrochemical reaction is believed to be oxidation of the supporting electrolyte rather than one involving SO_2. The oxidation of SO_2 occurs at potential beyond +5.0V vs. a silver quasi-reversible electrode.[94]

4-1-4 The Present Study

An important use of cyclic voltammetry is to determine whether a particular compound is oxidizable or reducible under certain conditions. The work described in this chapter was aimed at the measurement of the electrochemical properties of the compounds, described in the previous chapter, to determine the half-wave

potentials of the particular oxidation states in these compounds. When the half-wave potential for a particular couple is known, it is possible to choose a suitable oxidizing agent or reducing agent to convert the reduced form to the oxidized form or to convert the oxidized form to the reduced form. In particular we wished to determine whether the choice of solvents for the MoF_6/I^- redox reaction has any marked effect. The electrochemical properties of the Bu_4NMoF_6 salt and the ionic iodides, Bu_4NI and NaI, have been studied and comparisons of oxidizing and reducing abilities of these compounds in MeCN, CH_2Cl_2 and SO_2 have been made. The reference electrodes used were the Ag^+/Ag electrode for external application and ferrocene as an internal reference. The half-wave potential values obtained in the ferrocene referenced measurements were re-referenced to Ag^+/Ag through the relationship (4-4):

$$E_{\frac{1}{2}}X(vs.Ag^+/Ag) = E_{\frac{1}{2}}X(vs.Ferrocene) + E_{\frac{1}{2}}Ferrocene(vs.\ Ag^+/Ag) \qquad (4\text{-}4)$$

where $E_{\frac{1}{2}}X(vs.Ag^+/Ag)$ is the half-wave potential vs. Ag^+/Ag for the couple which was being studied, $E_{\frac{1}{2}}X(vs.Ferrocene)$ is the half-wave potential vs. ferrocene for the same couple as above and $E_{\frac{1}{2}}Ferrocene(vs.Ag^+/Ag)$ is the half-wave potential of ferrocene vs. Ag^+/Ag.

4-2 RESULTS AND DISCUSSION

4-2-1 Cyclic Voltammetric Studies in Acetonitrile.

The cyclic voltammogram of ferrocene (10^{-3} mol dm^{-3} in 0.1 mol dm^{-3} Bu_4NPF_6 MeCN solution) consists of a quasi-reversible wave. The half-wave potential, $E_{\frac{1}{2}}$ is + 0.055V vs. Ag^+(0.1 mol dm^{-3})/Ag, and the peak to peak separation, ΔEp, is 0.11V at a scan rate = 0.2 Vs^{-1}.

Cyclic voltammetry studies of MoF_6/MoF_6^-, MoF_6^-/MoF_6^{2-}, I_2/I_3^-, I_3^-/I^- and NO^+/NO couples were carried out in MeCN and the results are listed in Table 4-1.

The cyclic voltammogram of Bu_4NMoF_6 at a platinum electrode in MeCN consists of two quasi-reversible waves (Fig. 4-1). These two waves should be assigned to the couples MoF_6/MoF_6^- and MoF_6^-/MoF_6^{2-} for which the half-wave potentials are $E_{\frac{1}{2}}(MoF_6/MoF_6^-)$ = 1.58V, and $E_{\frac{1}{2}}(MoF_6^-/MoF_6^{2-})$ = -0.41V vs. Ag^+(0.1 mol dm^{-3})/Ag. These assignments were made by comparison with previous studies of $[Cu(MeCN)_4][MoF_6]$ in MeCN.[8] The peak to peak separation of these couples MoF_6/MoF_6^- and MoF_6^-/MoF_6^{2-} were 0.19V and 0.24V, respectively, at a scan rate of 0.20 Vs^{-1}. These values for the peak to peak separations indicate that the redox processes for MoF_6/MoF_6^- and MoF_6^-/MoF_6^{2-} couples on this time scale are not completely reversible (quasi-reversible). The cyclic voltammogram did not show any other wave in the potential range from +3.0V to -2.6V vs. Ag^+/Ag in MeCN.

The cyclic voltammogram of $NOMoF_6$ (Table 4-1) consists of three well defined quasi-reversible waves with half-wave potentials

Table 4-1 Half-wave potentials, $E_{\frac{1}{2}}$V vs. Ag^{+}(0.1 mol dm^{-3})/Ag in MeCN. Peak to peak separations in parentheses.

Solid species (10^{-2} ~ 10^{-3} mol dm^{-3})	Species in solution	MoF_6 / MoF_6^-	NO^+ / NO	I_2 / I_3^-	I_3 / I^-	MoF_6^- / MoF_6^{2-}
$NOMoF_6$	NO^+ + MoF_6^-	1.61 (0.18)	0.88 (0.28)			-0.34 (0.35)
$NOPF_6$	NO^+ + PF_6^-		0.83 (0.59)			
Bu_4NMoF_6	Bu_4N^+ + MoF_6^-	1.58 (0.19)				-0.41 (0.24)
Bu_4NI	Bu_4N^+ + I^-			0.30 (0.11)	-0.19 (0.34)	
NaI	Na^+ + I^-			0.32 (0.21)	-0.23 (0.53)	

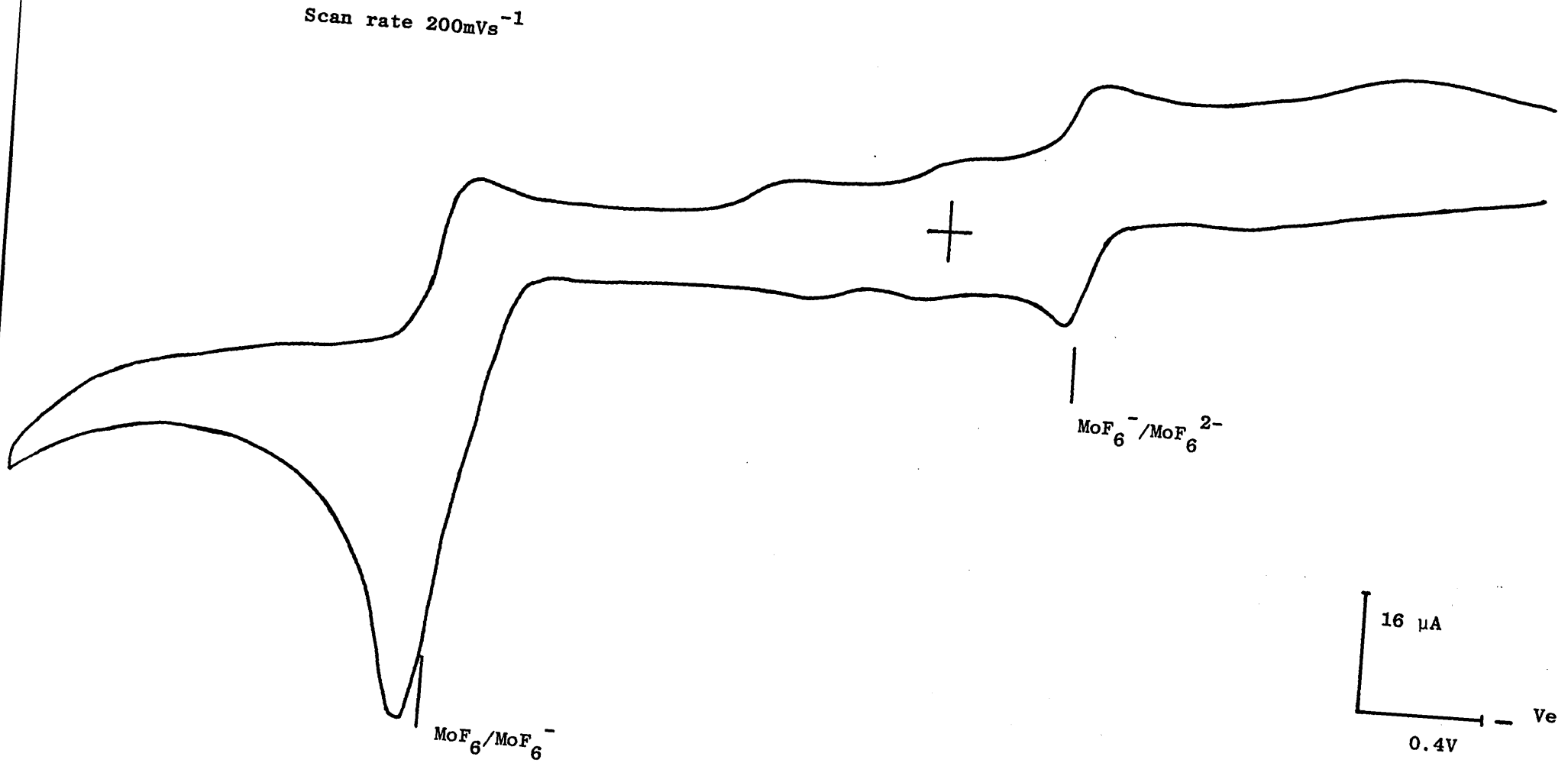


Figure 4-1: Cyclic voltammogram of Bu_4NMoF_6 in MeCN solution at 18°C.

+ 1.61V, + 0.88V, and -0.34V which should be assigned to the MoF_6/MoF_6^-, NO^+/NO, and MoF_6^-/MoF_6^{2-} couples respectively. The cyclic voltammogram of $NOPF_6$ was recorded and contained a quasi-reversible wave due to NO^+/NO couple whose half-wave potential is $E_{\frac{1}{2}}(NO^+/NO)$ = 0.83V vs. Ag^+/Ag. Anderson et al have found the half-wave potential, $E_{\frac{1}{2}}$ = + 0.87V for the couple NO^+/NO in $NOPF_6$ in MeCN as described above.[8] The difference in the half-wave potential values obtained in this work for NO^+/NO couple in different compounds $NOMoF_6$ and $NOPF_6$ may not be significant. This difference could arise from the different concentrations of the solutions for example.

The cyclic voltammogram of Bu_4NI at the platinum electrode in MeCN shows an irreversible wave due to I_3^-/I^- and a quasi-reversible wave due to I_2/I_3^- with anodic and cathodic peak separations of 0.34 and 0.11V, respectively, (Fig 4-2). The half-wave potentials of these couples were found to be $E_{\frac{1}{2}}(I_2/I_3^-)$ = 0.30V and $E_{\frac{1}{2}}(I_3^-/I^-)$ = -0.19V vs. Ag^+/Ag. Similarly for NaI, these half-wave potentials were found to be $E_{\frac{1}{2}}(I_2/I_3^-)$ = 0.32V and $E_{\frac{1}{2}}(I_3^-/I^-)$ = -0.23V vs. Ag^+/Ag. Although the half-wave potentials for the couples in Bu_4NI and NaI appear to be slightly different, these differences may not be significant and the situation is similar to the NO^+/NO case.

The data for hexafluoromolybdates and iodides show that the half-wave potential for the MoF_6^-/MoF_6^{2-} couple is more negative than that of the I_3^-/I^- couple. This indicates that iodides such as Bu_4NI and NaI will not reduce MoF_6^- salts to MoF_6^{2-} salts in MeCN under conditions where their concentrations are similar.

Scan rate 200mVs^{-1}

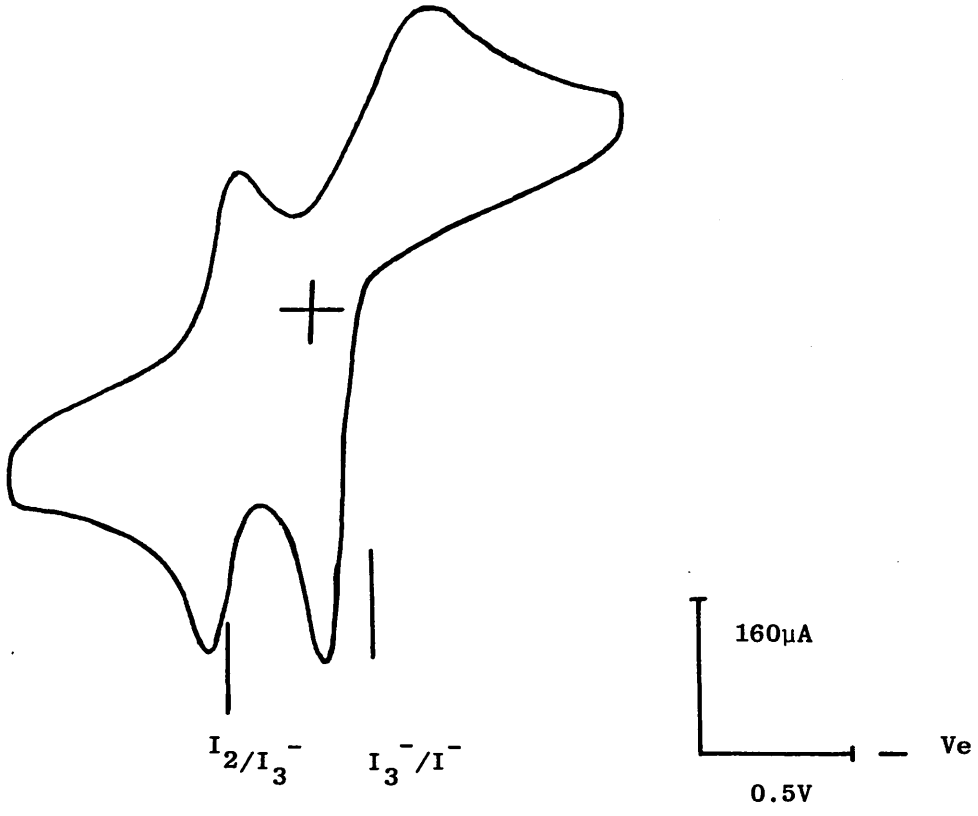


Figure 4-2: Cyclic voltammogram of Bu_4NI in MeCN solution at 18^{o}C.

4-2-2 Cyclic Voltammetry Studies in Dichloromethane

Most of the cyclic voltammetric studies in CH_2Cl_2 were carried out with ferrocene as an internal reference. The half-wave potential of ferrocene in CH_2Cl_2 is 0.10V vs. Ag^+/Ag.[80] The values of the half-wave potential obtained in this solvent are listed in Table 4-2.

Two quasi-reversible waves are present in the cyclic voltammogram of Bu_4NMoF_6 at a platinum electrode in CH_2Cl_2. These two waves with half-wave potentials, $E_{\frac{1}{2}}$ of 1.52V and -0.43V vs. Ag^+/Ag are assigned to the couples MoF_6/MoF_6^- and MoF_6^-/MoF_6^{2-} respectively by comparison with the study of this salt in MeCN. The observed reductions of MoF_6 to the +5 and +4 species in CH_2Cl_2 occur at slightly less positive half-wave potential values compared to those in MeCN.

Similar to the cyclic voltammogram of Bu_4NI in MeCN, the cyclic voltammogram of Bu_4NI at platinum electrode in CH_2Cl_2 also contains two waves, although the anodic peaks are not as well defined as those in MeCN (Fig. 4-3). These observations suggest that the electron transfer processes (equation 4-1 and 4-2) in the anodic sweep are extremely sluggish. The waves due to I_3^-/I^- and I_2/I_3^- couples occurred with anodic and cathodic peak separation of 1.14 and 0.58V respectively. The half-wave potentials of these couples are $E_{\frac{1}{2}}(I_2/I_3^-)$ = 0.47V and $E_{\frac{1}{2}}(I_3^-/I^-)$ = -0.18V vs. Ag^+/Ag. No data were obtained for NaI in CH_2Cl_2 because of its insolubility. In CH_2Cl_2, Bu_4NI has no capability of reducing MoF_6^- to MoF_6^{2-} according to the half-wave potential values for these compounds.

Table 4-2 Half-wave potentials, $E_{\frac{1}{2}}V$ vs. Ag^{+}/Ag in CH_2Cl_2.

Peak to peak separations in parentheses.

Solid species ($10^{-2} \sim 10^{-3}$ mol dm^{-3}).	Species in solution	MoF_6 / MoF_6^{2-}	I_2 / I_3^-	I_3^- / I^-	MoF_6^- / MoF_6^{2-}
Bu_4NMoF_6	Bu_4N^+ + MoF_6^-	1.52 (0.15)			-0.43 (0.28)
Bu_4NI	Bu_4N^+ + I^-		0.47 (0.58)	-0.18 (1.14)	

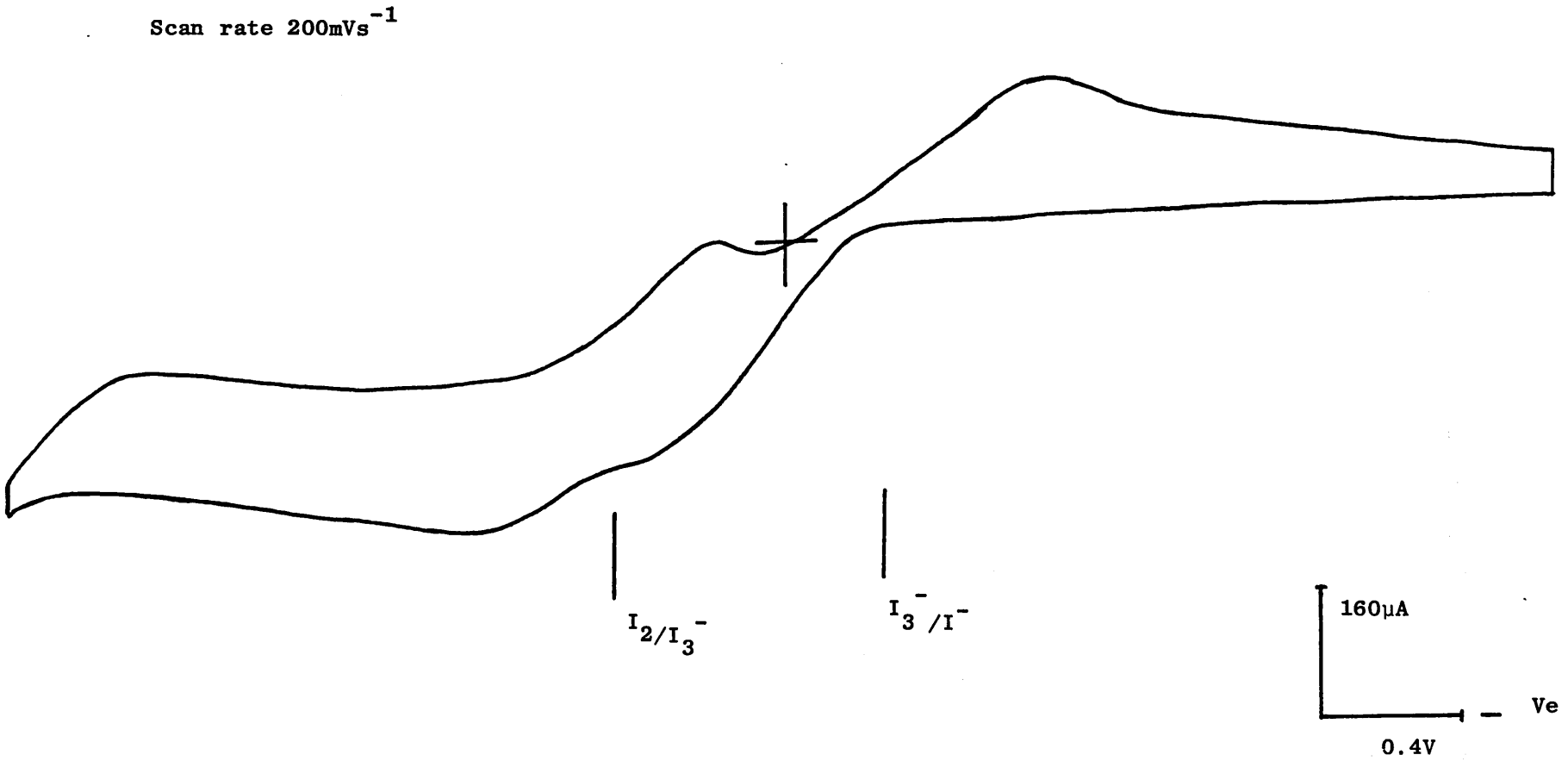


Figure 4-3: Cyclic voltammogram of Bu_4NI in CH_2Cl_2 solution at 18°C.

4-2-3 Cyclic Voltammetric Studies in Liquid Sulphur Dioxide.

The cyclic voltammogram of Bu_4NMoF_6 at platinum electrode in liquid SO_2 contained one quasi-reversible wave in the accessible region (Fig. 4-4). By comparison with the study of this salt in MeCN and CH_2Cl_2, this wave should be assigned to the couple MoF_6/MoF_6^-. The cathodic peak of the wave which was due to the couple MoF_6^-/MoF_6^{2-} could not be observed since it is outside the accessible range. The half-wave potential of MoF_6/MoF_6^- is + 1.41V vs. Ag^+/Ag with a peak to peak separation of 0.22V at a scan rate of $0.20Vs^{-1}$.

4-2-4 Comparison Among the Three Solvents.

The half-wave potentials of the couples MoF_6/MoF_6^- and MoF_6^-/MoF_6^{2-} are slightly different in different solvents, although these differences may not be significant. However the solvent properties should have some effect on the redox properties of the compounds. According to the data obtained, it appears that the values of the half-wave potentials become less positive when the nature of the solvent changes from a relatively strong electron donor solvent, MeCN, to a predominantly electron acceptor solvent, SO_2, via the intermediate solvent, CH_2Cl_2 (Table 4-3).

On the basis of the half-wave potential in the three solvents, the oxidizing ability of MoF_6 appears to decrease in the order $MeCN>CH_2Cl_2>SO_2$. Although the cathodic peak of the wave due to MoF_6^-/MoF_6^{2-} couple is not observed in liquid SO_2, according to the value of the half-wave potential for MoF_6^-/MoF_6^{2-} couple in the other two solvents the half-wave potential of this couple

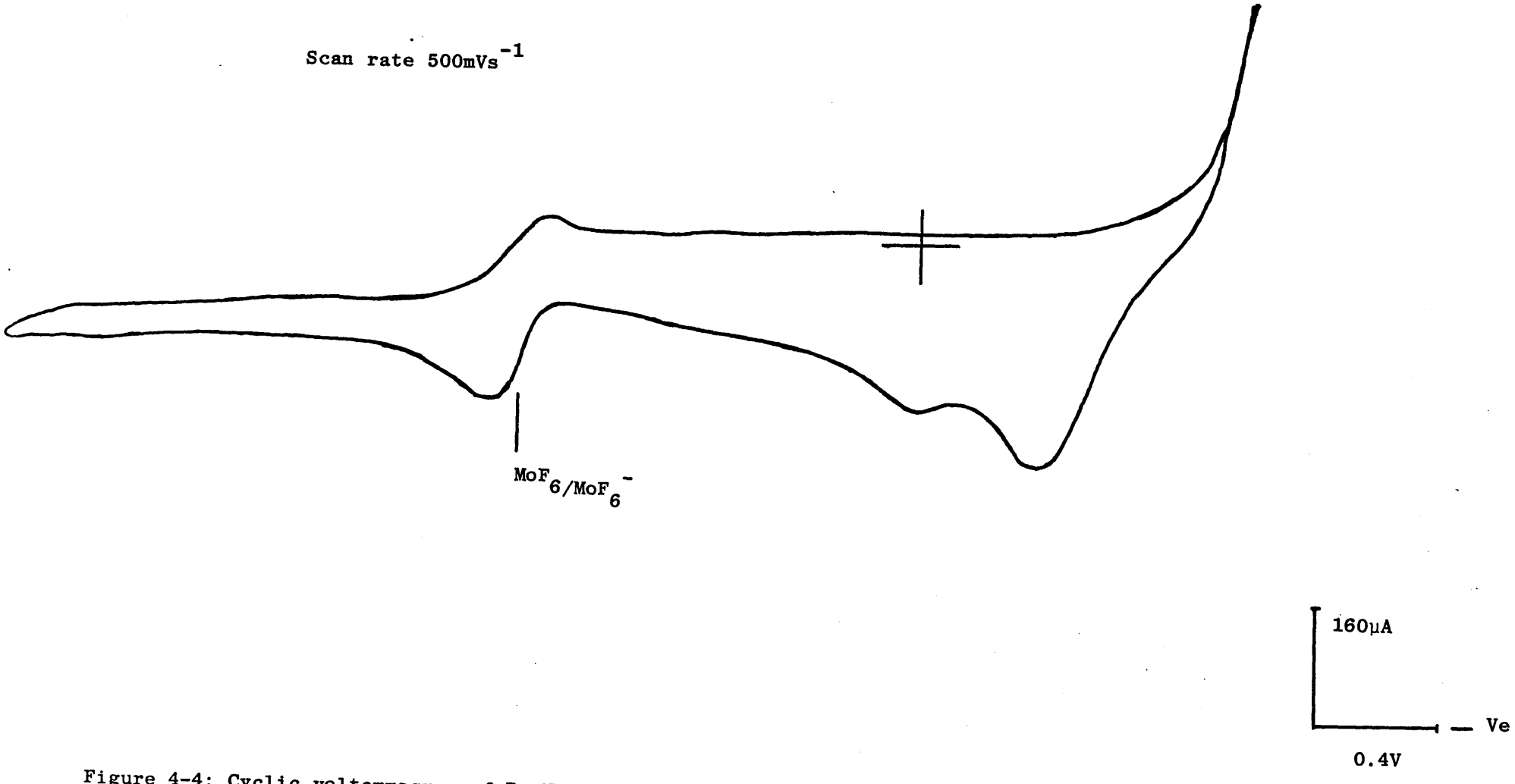


Figure 4-4: Cyclic voltammogram of Bu_4NMoF_6 in liquid SO_2 solution at -40^{o}C

Table 4-3 Comparison among the half-wave potentials of the couples MoF_6/MoF_6^- and MoF_6^-/MoF_6^{2-} in MeCN, CH_2Cl_2 and liquid SO_2 ($E_{\frac{1}{2}}$V vs. Ag^+/Ag).

	MeCN	CH_2Cl_2	SO_2
MoF_6/MoF_6^-	1.58	1.52	1.41
MoF_6^-/MoF_6^{2-}	-0.41	-0.43	-

would be expected to lie between -0.42 ~ -0.45V vs. Ag^+/Ag. For the iodide case, the shape of the voltammogram of Bu_4NI in MeCN and CH_2Cl_2 is different. In MeCN, the anodic peaks appear at less positive positions compared to those in CH_2Cl_2. From the shapes of the voltammograms, the couples I_3^-/I^- and I_2/I_3^- have relatively faster rates of electron transfer at a platinum electrode in MeCN than in CH_2Cl_2, since the peak to peak separations are smaller in MeCN than in CH_2Cl_2. An anodic shift in the peak potential for the I_3^-/I^- couple occurs when the concentration of SO_2 in propylene carbonate is increased. This is due to the formation of ISO_2^- as described previously.[93] A related effect may occur in MeCN where specific interaction involving I_2 and MeCN is possible.

According to the data obtained Bu_4NI would not be expected to reduce MoF_6^- to MoF_6^{2-} in MeCN and CH_2Cl_2. However if the difference of the half-wave potentials of the two couples is relatively small, the direction of the reaction cannot be predicted by simply comparing the half-wave potentials of the couple. In this case, the effect of the concentration of the species should be considered. Therefore, although the half-wave potential of I_3^-/I^- is slightly less negative than that of MoF_6^-/MoF_6^{2-} in the comparable concentrations of $[MoF_6^-]$ and $[I^-]$, were $[I^-]$ to be much larger than $[MoF_6^-]$, the reduction of MoF_6^- to MoF_6^{2-} would be a possibility. This explains the need for a very soluble I^- to perform the reaction satisfactorily.

4-3 CONCLUSION

The cyclic voltammetry study shows that the iodide Bu_4NI is unlikely to reduce MoF_6^- salts to MoF_6^{2-} salts in MeCN and CH_2Cl_2. The half-wave potential of the MoF_6/MoF_6^- couple appears to become less positive as the electron donor ability of solvent decreases.

As in previously reported work, the cyclic voltammetric study of the iodides shows that iodide is oxidized to I_2 in two electrochemical steps; firstly triiodide is formed and then the oxidation proceeds to iodine (equations 4-1 and 4-2).

4-4 EXPERIMENTAL

The detailed experimental procedure for cyclic voltammetry study was described in Chapter Two. The preparation of Bu_4NMoF_6 was described in Chapter Three.

The compound $NOMoF_6$ was prepared as follows.[39] Acetonitrile (5 cm^3) was distilled into a previously evacuated and flamed out double limb reaction vessel. Molybdenum hexafluoride (1 mmol) was added into the reaction vessel, then nitric oxide, NO (1.5 mmol) was distilled into the vessel. The reaction mixture was allowed to warm slowly to room temperature. An orange solid was obtained from the resulting solution after removal of volatile materials. The infrared spectrum of the product contained bands at 620 cm^{-1} (ν_3) and 240 cm^{-1} (ν_4) due to MoF_6^- and at 2340 cm^{-1} due to ν(NO) of NO^+. The orange solid was thus identified as nitrosonium hexafluoromolybdate(V) ($NOMoF_6$).

CHAPTER FIVE

REACTIONS OF MOLYBDENUM AND TUNGSTEN HEXAFLUORIDES WITH THE METALS Mo AND W IN ACETONITRILE.

5-1 INTRODUCTION

A number of transition metal pentafluorides form 1:1 and 1:2 complexes with organic ligands for example, MF_5L (M = Nb or Ta, L = Me_2SO, EtCN or CH_2ClCN), TaF_5(2-Me-py), MoF_5L (L = MeCN or CH_2ClCN) and $TaF_5(4\text{-Me-py})_2$.[51] The 1:1 complexes, for example MoF_5.NCMe, are particularly relevant to this work. The 1:1 complexes are proposed to be monomeric in the solid state with a symmetry of C_{4v}.[51] Their preparations were carried out by the interaction of the parent molecules, metal pentafluorides and organic ligands.

Although MoF_5.NCMe was prepared by the simple reaction between MoF_5 and the solvent MeCN at room temperature, the preparation of MoF_5 by reduction of MoF_6 with Mo metal in a bomb at 140°C is time consuming. A number of preparative methods of MoF_5 have been reported (see Chapter One), but most of these syntheses have been found to give poor yields and impure products and to be generally unreliable,[9] or the handling of some of the reagents is not convenient and the reactions are slow.

The compound WF_5 is known to be unstable with respect to the disproportionation reaction to give WF_6 and WF_4. The preparation of its complex with MeCN has not been reported. Formation of the species WF_5.NCMe has been postulated in MeCN solution from the F^- ion transfer reaction.[8]

$$WF_6^- + WF_6 \underset{\text{MeCN}}{\rightleftharpoons} WF_7^- + WF_5.NCMe \qquad (5\text{-}1)$$

While the present work was in progress a fellow student Laurence McGhee prepared a compound characterized as $[TeF_3(NCMe)_2][MoF_6]$, $3MoF_5$.NCMe by oxidation of Te using MoF_6 in MeCN.[95]

The vibrational spectra of acetonitrile[96,97] and its 1:1 adducts are well known.[73,98,99] Fuggle et al first prepared MoF_5NCMe and studied the vibrational spectrum of this complex and have made partial assignments for the spectrum on the basis of C_{4v} symmetry.[69] Later Shriver and co-workers provided the most complete spectroscopic data and assignments for molecules of the same symmetry : acetonitrile complexes of group Va pentafluorides, for example AsF_5.NCMe and SbF_5.NCMe.[73,98] These complexes are reported to have approximate C_{4v}symmetry about the central atom. It is assumed that the molecule, SbF_5NCMe has a non-rigid structure in which the methyl group rotates freely with respect to the four equatorial fluorine atoms. The absorption frequencies attributed to the SbF_5 and $NCCH_3$ moieties in the molecule are rather widely separated, and the SbF_5 portion and $NCCH_3$ part of the complex are spatially remote. Shriver and coworkers have reported that the molecule SbF_5.$NCCH_3$ with the C_{4v} symmetry has 21 vibrational modes in which $4A_1$ + 4E fundamentals (ν_1, ν_2, ν_3, ν_4, ν_{13}, ν_{14}, ν_{15}, and ν_{17}) are attributed to the acetonitrile portion ($\sim C_{3v}$) and $4A_1 + 2B_1 + 1B_2 + 4E$ modes (ν_5, ν_6, ν_7, ν_8, ν_{10}, ν_{11}, ν_{12}, ν_{16}, ν_{18}, ν_{19} and ν_{20}) are due to the SbF_5N portion ($\sim C_{4v}$). In addition there is an SbNC deformation belonging to the species E and an A_2 torsional mode.[98]

The purpose of the work described in this Chapter was to find a convenient method to reduce MF_6 (M = Mo, W) to pentavalent complexes. The compounds isolated were identified by comparison of their infrared spectra with the literature reports of MoF_5NCMe and related complexes and are discussed in terms of the previously proposed structure for monomeric MF_5L having C_{4v} symmetry. All

the detailed assignments for the bands in infrared spectra were made on the basis of those made for the molecule SbF_5NCMe.[98]

5-2 RESULTS AND DISCUSSION

5-2-1 The Preparation of the complex MoF_5.NCMe

Molybdenum pentafluoride was prepared by the reduction of MoF_6 using Mo metal powder at 150°C in the reaction bomb. A bright yellow solid, which was much less volatile than MoF_6, was obtained. Purified MeCN was added to $(MoF_5)_4$ to give the complex MoF_5.NCMe. The solid MoF_5.NCMe is pale yellow, non-volatile and very hygroscopic. The solid state infrared spectrum of the product was recorded and is given in Table 5-1. Comparison with previously reported work[51] indicates that the spectrum is identical to that in the literature. The frequencies of infrared spectrum of liquid MeCN are shown in Table 5-2 for comparison. This preparation of MoF_5.NCMe is time consuming and the product was often contaminated by hydrolysis products, for example $MoOF_4$.NCMe.

The above reaction can be carried out in one step at room temperature by the reduction of MoF_6 using Mo metal powder in MeCN. The reaction occurs readily and a pale yellow solid was isolated from the solution. The solid is very moisture sensitive and rapidly became blue when it was exposed to moist air. The elemental analysis of the solid is listed in Table 5-3 and corresponds to MoF_5.NCMe. The product is stable at room temperature in the absence of moisture. According to the analysis, the reaction is as described in equation 5-2 as expected.

$$Mo + 5MoF_6 + 6MeCN \longrightarrow 6MoF_5.NCMe \qquad (5\text{-}2)$$

Table 5-1 Infrared spectrum of solid $MoF_5.NCMe$ [from $(MoF_5)_4$ + MeCN]

Frequencies $\nu_{max}(cm^{-1})$		Assignment[98]
Present work	Previous work[69]	
3010 w	3020 m	ν_{13} CH_3 str. E
2944 m	2952 ms	ν_1 CH_3 str. A_1
2322 s	2322 m	ν_2 CN str. A_1
2297 ms	2297 s	$\nu_3 + \nu_4$
2255 vw	2255 w	$\nu_1-\nu_{16}$; $\nu_1-\nu_6$
1028 mw	(1028,1015) mw	ν_{15} CH_3 rock. E
953 w	953 m	ν_4 CC str. A_1
720 s	720 w	$2\nu_{12}+\nu_{19}$; $\nu_3-\nu_7$; $\nu_{14}-\nu_{16}$
703 m	703 mw	ν_5 MoN str. A_1
650 vs	650 vs	ν_6 MoF' axial str. A_1
635 sh	635 sh	ν_7 MoF_4 equatorial str. A_1
418 w	418 w	ν_{17} CCN def. E
285 ms	285 m	ν_{18} F'-MoF_4 def. E
250 s	250 m	ν_{19} MoF_4 in-plane def. E

vs = very strong; s = strong; sh = shoulder; m = medium

w = weak; ms = medium strong; mw = medium weak; vw = very weak

str. = stretch; def.= deformation

Table 5-2 Infrared spectrum of free MeCN.

Frequencies ν_{max} (cm^{-1})	Assignment[58]	
3164 w	$\nu_2 + \nu_4$	A_1
3003 m	ν_5 C-H str.	E
2944 m	ν_1 C-H str.	A_1
2628 w	$\nu_2 + \nu_8$	E
2411 w	$\nu_3 + \nu_7$	E
2293 m	$\nu_3 + \nu_4$	A_1
2254 s	ν_2 C≡N str.	A_1
1443 s	ν_6 CH_3 def.	E
1376 s	ν_3 CH_3 def.	A_1
1047 s	ν_7 CH_3 rock.	E
917 s	ν_4 C-C str.	A_1
749 m	$2\nu_8$	A_1
379 m	ν_8 C-C≡N bend	E

str. = stretch; def. = deformation

s = strong m = medium w = weak

The solid state infrared spectrum of the product was recorded and the data are listed in Table 5-4.

5-2-2 Reaction of Tungsten Metal with WF_6 in MeCN.

The reduction of WF_6 with tungsten metal in MeCN was slow at room temperature. After the mixture was shaken overnight a pale yellow solid was isolated, which was very moisture sensitive and became blue when it was exposed to the moist atmosphere. The elemental analysis was made and the results are shown in Table 5-3. According to the analysis, the reduction of WF_6 by tungsten metal produced WF_5.NCMe as described in equation 5-3.

$$W + 5WF_6 + 6MeCN \longrightarrow 6WF_5.NCMe \qquad (5\text{-}3)$$

The infrared spectrum was studied and the spectroscopic data are listed in Table 5-4

5-2-3 Comparisons of Infrared Spectroscopic Data

According to the assignment for the spectrum of SbF_5.NCMe,[98] in the MoF_5.NCMe and WF_5.NCMe molecules, the acetonitrile portion shows the fundamentals ν_1, ν_2, ν_3, ν_4, ν_{13}, ν_{14}, ν_{15} and ν_{17}, and the MF_5N (M = Mo, W) portion shows five fundamental vibrations (ν_5, ν_6, ν_7, ν_{18} and ν_{19}) in the region 4000 - 200 cm^{-1}, although as expected some of them have different positions from those of SbF_5.NCMe. In addition, there are several combination bands observed in this region. All spectra were obtained at room temperature.

Table 5-3 Elemental analysis of MoF_6.NCMe and WF_5.NCMe.

Elements		C	H	F	N	Mo
MoF_5.NCMe	Req.(%)	10.4	1.3	40.9	6.0	41.35
	Found (%)	10.1	1.15	40.8	6.0	41.0
WF_5.NCMe	Req.(%)	7.5	0.95	29.7	4.4	
	Found (%)	7.6	0.7	29.4	4.35	

Table 5-4 Infrared spectrum of solid MoF_5.NCMe and WF_5.NCMe ($M+5MF_6+6MeCN$) (M = Mo, W)

Frequencies $\nu_{max}(cm^{-1})$		Assignment[98]	
MoF_5.NCMe	WF_5.NCMe		
3010 w	3010 w	ν_{13} CH_3 str.	E
2944 m	2944 mw	ν_1 CH_3 str.	A_1
2322 s	2319 ms	ν_2 CN str.	A_1
2297 ms	2297 ms	$\nu_3 + \nu_4$	
2255 vw		$\nu_1-\nu_{16}$; $\nu_1-\nu_6$	
1410 w	1410 w	ν_{14} CH_3 def.	E
1364 w	1365 w	ν_3 CH_3 def.	A_1
1028 mw	1026 m	ν_{15} CH_3 rock.	E
953 w	942 w	ν_4 CC str.	A_1
720 s	720 ms	$2\nu_{12}+\nu_{19}$; $\nu_3-\nu_7$; $\nu_{14}-\nu_{16}$	
703 m	703 ms	ν_5 MN str.	A_1
650 vs	640 vs	ν_6 MF′ axial str.	A_1
635 sh	610 sh	ν_7 MF_4 equatorial str.	A_1
418 w	418 w	ν_{17} CCN def.	E
285 ms	270 s	ν_{18} F′-MF_4 def.	E
250 s	240 s	ν_{19} MF_4 in-plane def.	E

w = weak; s = strong; m = medium; vs = very strong; ms = medium strong

mw = medium weak; vw = very weak; sh = shoulder; str = stretch

def. = deformation

(i) Spectrum of MoF_5.NCMe

The infrared spectrum of deuterated complex, $MoF_5.NCCD_3$, was also studied (Table 5-5). For comparison, the infrared fundamental frequencies of liquid CD_3CN are also shown in Table 5-5. The comparison of the spectra of the CH_3CN and CD_3CN portion of the molecule are made with support of the previous work.[98,99] Table 5-6 shows the fundamentals of infrared spectra for both CH_3CN and CD_3CN in liquid phase.

The fundamentals ν_1 (symmetric CH_3 stretch A_1), ν_2 (CN stretch A_1) and ν_{13} (asymmetric CH_3 stretch E) lie in the region 4000 - 2000 cm^{-1}. The fundamental ν_1, which is observed at about 2944 cm^{-1} for the normal isotopic species (H) and at about 2118 cm^{-1} for deuterated species (D), is a medium intensity band in the infrared spectrum. The ν_{13} fundamental vibration appears with weak intensity in the H isotopic spectrum at about 3010 cm^{-1} and with very weak intensity in D isotopic spectrum at about 2260 cm^{-1}. The ν_1 and ν_{13} are close to the values found for free acetonitrile. The vibration ν_2 (CN stretch, A_1) has a strong intensity sharp band in infrared spectrum at 2322 cm^{-1} with an increase of about 68 cm^{-1} from free acetonitrile in the normal isotopic spectrum. This vibration is observed at 2310 cm^{-1} with strong intensity for deuterated species, and the frequency increased about 43 cm^{-1} from that of free CD_3CN.

There are a number of bands which may be attributed to combination bands. The H isotopic molecules show a satellite peak of medium strong intensity to the low frequency side (2297 cm^{-1}) of the ν_2 vibration. This may be attributed to the combination band $\nu_3 + \nu_4$ in Fermi resonance with ν_2. The satellite peak is virtually

Table 5-5 Infrared spectra of solid $MoF_5.NCCD_3$ and fundamental frequencies of liquid CD_3CN.

$MoF_5.NCCD_3$		CD_3CN		Type of motion.
Frequencies $\nu_{max}(cm^{-1})$	Assignment	Frequencies $\nu_{max}(cm^{-1})$	Assignment[97]	
2310 s	ν_2 A_1	2267 s	ν_2 A_1	C≡N str.
2260 vw	ν_{13} E	2220 sh	ν_5 E	CD_3 str.
2118 m	ν_1 A_1	2125 m	ν_1 A_1	CD_3 str.
-	ν_3 A_1	1105 m	ν_3 A_1	CD_3 def.
1018 m	ν_{14} E	1040 s	ν_6 E	CD_3 def.
-	ν_{15} E	847 sh	ν_7 E	CD_3 rock
867 m	ν_4 A_1	833 s	ν_4 A_1	CC str.
720 ms	$2\nu_{12}+\nu_{19}$			comb.
	$\nu_3 - \nu_7$			
	$\nu_{14}-\nu_{16}$			
703 m	ν_5 A_1			MoN str.
650 s	ν_6 A_1			MoF' axial str.
635 sh	ν_7 A_1			MoF_4 equatorial str.
-	ν_{17} E	-	ν_8 E	CCN def.
285 sh	ν_{18} E			$F'-MoF_4$ def.
250 s	ν_{19} E			MoF_4 in-plane def.

s = strong; m = medium; w = weak; sh = shoulder vw = very weak

ms = medium strong; str. = stretch def. = deformation

Table 5-6 Fundamental frequencies of infrared spectra of CH_3CN and CD_3CN (Both are liquid phase)

$CH_3CN(cm^{-1})$	CD_3CN (cm^{-1})	Assignment[97]	
2944 m	2125 m	ν_1 C-H str.	A_1
2254 s	2267 s	ν_2 C≡N str.	A_1
1376 s	1105 m	ν_3 CH_3 def.	A_1
917 s	833 s	ν_4 C-C str.	A_1
3003 m	2220 sh	ν_5 C-H str.	E
1443 s	1040 s	ν_6 CH_3 def.	E
1047 s	847 sh	ν_7 CH_3 rock.	E
379 m	?	ν_8 C-C≡N bend	E

s = strong; m = medium; sh = shoulder

str. = stretch def. = deformation

absent in the deuterated molecule.

Except for ν_{17} (CCN deformation) the remaining acetonitrile fundamentals fall within the region 2000 - 800 cm^{-1}. For the H isotopic molecules four bands ν_3 (CH_3 deformation A_1), ν_4 (CC stretch A_1) ν_{14} (CH_3 deformation, E) and ν_{15} (CH_3 rock, E) occur between 950 and 1450 cm^{-1}. The vibration ν_3 appears at 1364 cm^{-1} and the frequency decreased by 12 cm^{-1} compared with that of the CH_3 deformation in free acetonitrile, 1376 cm^{-1}. The weak peak at 1410 cm^{-1} of the infrared spectrum is assigned to the vibration ν_{14}. This band exhibits a decrease of 33 cm^{-1} from that of free acetonitrile. For the deuterated complex the ν_{14} mode is observed at 1018 cm^{-1}, although the ν_3 mode is not found for deuterated complex, and the frequency of ν_{14} mode decreases about 22 cm^{-1} compared with free deuterioacetonitrile. The frequency of the vibration ν_4 shows an increase of about 36 cm^{-1} to 953 cm^{-1} from the CC stretching frequency of free acetonitrile. In the case of the deuterated complex, the ν_4 vibrational band is found at 867 cm^{-1} with an increase of 34 cm^{-1} compared to this vibration of free deuterioacetonitrile. The vibration ν_{15} (CH_3 rock, E) appears in the infrared spectrum at 1028 cm^{-1} for H isotopic complex with a decrease of 19 cm^{-1} from the CH_3 rock of free acetonitrile. However this band is not observed in the spectrum of the D isotopic complex.

The vibrations involving the central metal atom appear in the region below 800 cm^{-1}. Both MoF and MoN stretching frequencies are observed in the region 800-600 cm^{-1}. However the MoF stretching frequencies dominated the region of the spectrum. The MoN stretching mode ν_5 is observed at about 703 cm^{-1} with medium strong intensity

and a very strong band occurs at about 650 cm^{-1} which is assigned to the MoF' axial stretch (ν_6) in the infrared spectrum. The MoF_4 equatorial stretch ν_7 appears as a shoulder to the low frequency side (635 cm^{-1}) of the MoF' axial stretch.

The only observed fundamental which is due to acetonitrile portion is ν_{17} (CCN deformation, E), and occurs at about 418 cm^{-1} for normal isotopic H complex in 600 - 200 cm^{-1} region. This fundamental frequency shows an increase of 39 cm^{-1} in the complex compared to that of free CH_3CH(379cm^{-1}). For the D isotopic molecules, the vibration ν_{17} is not observed in the spectrum.

The deformation modes fall in the region below 300 cm^{-1}. Two deformations (F'-MoF_4 deformation, E and MoF_4 in plane deformation, E), which are observed in the region 300 - 200 cm^{-1}, are ν_{18} and ν_{19} and appear at about 285 and 250 cm^{-1}.

The frequencies of infrared spectra of MoF_5.NCMe and MoF_5.$NCCD_3$ are compared in Table 5-7.

(ii) Spectrum for WF_5.NCMe

The absorption frequencies attributed to the WF_5 and MeCN portions in the molecule are very similar to those in MoF_5.NCMe (Table 5-4). The spectrum also was obtained at room temperature. The fundamentals ν_1, ν_3, ν_{14} and ν_{13} for acetonitrile portion and ν_5 for WN stretch are appearing at the same positions as those of MoF_5.NCMe. All frequencies of other fundamentals observed in the infrared spectrum in the region 4000 - 200 cm^{-1} have slight shifts towards the lower frequency direction compared with those of MoF_5.NCMe. The CN stretching mode ν_2, observed at 2322 cm^{-1}

Table 5-7 Infrared spectra of MoF_6.NCMe and MoF_5.$NCCD_3$ in solid state

Frequencies $\nu_{max}(cm^{-1})$		
MoF_5.$NCCH_3$	MoF_5.$NCCD_3$	Assignment[98]
3010 w	2260 vw	ν_{13} CH_3 str. E
2944 m	2118 m	ν_1 CH_3 str. A_1
2322 s	2310 s	ν_2 CN str. A_1
2297 ms	-	$\nu_3 + \nu_4$
2255 vw	-	$\nu_1-\nu_{16}$; $\nu_1-\nu_6$
1410 w	1018 m	ν_{14} CH_3 def. E
1364 w	-	ν_3 CH_3 def. A_1
1028 mw	-	ν_{15} CH_3 rock. E
953 w	867 w	ν_4 CC str. A_1
720 s	720 ms	$2\nu_{12}+\nu_{19}$; $\nu_3-\nu_7$; $\nu_{14}-\nu_{16}$
703 m	703 m	ν_5 MoN str. A_1
650 vs	650 s	ν_6 MoF′ axial str. A_1
635 sh	635 sh	ν_7 MoF_4 equatorial str. A_1
418 w	-	ν_{17} CCN def. E
285 ms	285 sh	ν_{18} F′-MoF_4 def. E
250 s	250 s	ν_{19} MoF_4 in-plane def E

for MoF_5.NCMe, appears at 2319 cm^{-1} for the tungsten complex. In general, the fundamentals involving metal fluorine vibrations (ν_6, ν_7, ν_{18} and ν_{19}) are shifted 10-25 cm^{-1} towards low frequency.

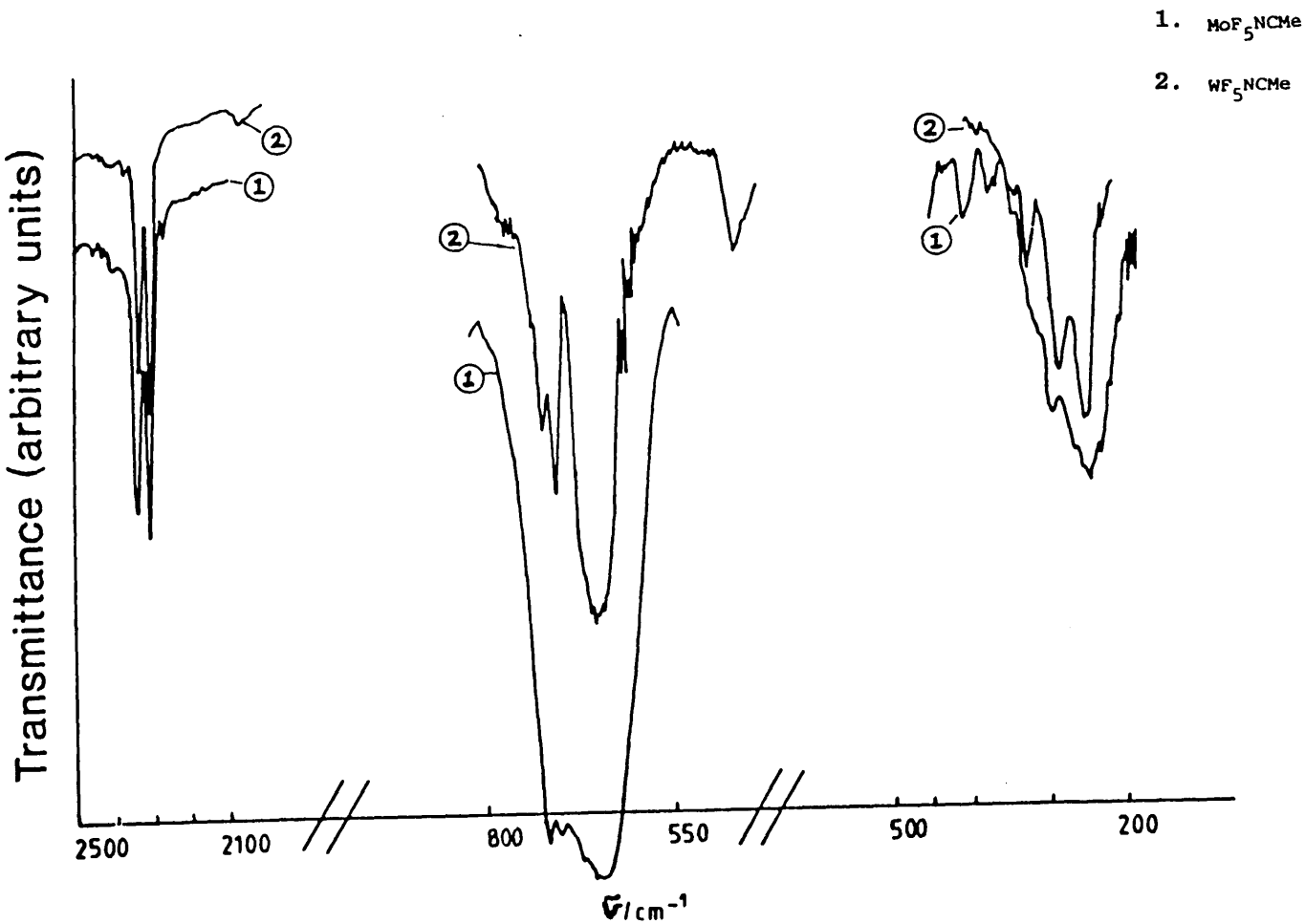
Although tungsten pentafluoride, which has a tetrameric structure with linear bridging fluorine atoms, is known to be unstable with respect to the disproportionation to WF_6 and WF_4 even at room temperature,[100] the product WF_5.NCMe produced in this work is quite stable at room temperature in the absence of moisture. The decomposition reaction of tungsten pentafluoride involves electron transfer. The relative stability of WF_5.NCMe compared with $(WF_5)_4$ may be due to the relatively stronger electron donor ability of MeCN molecule compared with a F ligand. The tungsten(V) in the unstable tungsten pentafluoride could be solvated by MeCN and appears to be stabilized by the supply of the lone pair of electrons on the nitrogen atom of MeCN.

The infrared spectra of the two compounds MoF_5.NCMe and WF_5.NCMe are shown in Figure 5-1.

5-2-4 Reaction of Tungsten Metal with MoF_6 in Acetonitrile.

The hexafluoride MoF_6 can be reduced by tungsten metal powder at room temperature in MeCN. Although the reaction was slower than that of MoF_6 and Mo, it was much faster than the reaction of W and WF_6. The yield was also greater than that from the reaction of W and WF_6. A pale yellow solid product was isolated. Previous work has shown that MoF_6 is a stronger oxidizing agent than WF_6.[8]

Figure 5-1 Infrared spectra of MoF_5.NCN and WF_5.NCMe



Tungsten hexafluoride can oxidize W metal at room temperature in MeCN as described in section 5-2-2, so MoF_6 should be capable of oxidizing W metal to W^V in MeCN. The product was therefore expected to be a mixture of Mo^V and W^V complexes. The mole ratio WF_5:MoF_5 should be 1:5 in the product, since one mole of W can reduce five moles of MoF_6 according to the equation 5-4.

$$5MoF_6 + W + \xrightarrow{MeCN} 5MoF_5.NCMe + WF_5.NCMe \qquad (5\text{-}4)$$

The analysis of the product was carried out by microanalyses for C, H and N and atomic absorption spectroscopy for Mo. The data are shown in Table 5-8. The analytical result fitted the formulation of $WF_5.5MoF_5.8MeCN$.

The infrared spectrum (Table 5-9) of the solid was recorded and is very similar to the spectrum of the species with the symmetry of C_{4v}. Most of the bands are closer to those of $MoF_5.NCMe$ rather than to $WF_5.NCMe$ (Table 5-4). The major difference in this spectrum from those of $MoF_5.NCMe$ and $WF_5.NCMe$ is that some sharp bands due to acetonitrile portion appear twice in the spectrum. For example, C≡N stretching vibration ν_2 appears at 2322 cm^{-1}, and there is a small shoulder to the low frequency side of this band at 2319 cm^{-1}. These two frequencies may be due to the C≡N stretching vibration in different molecules, $MoF_5.NCMe$ and $WF_5.NCMe$ respectively. The mode ν_{15}, which is the CH_3 rocking vibration, is observed at 1028 cm^{-1} for $MoF_5.NCMe$ and at 1026 cm^{-1} for $WF_5.NCMe$, while in the mixed reaction product there is a band at 1019 cm^{-1} accompanied by a small shoulder at 1028 cm^{-1}. Similarly the C-C stretch (ν_4) occurs at 953 and 941 cm^{-1} and these

Table 5-8 Elemental analysis for the product from the reaction of MoF_6 and W in MeCN.

Elements	C	H	N	Mo
Req. (%) As $WF_5.5MoF_5.8MeCN$	12.3	1.55	7.2	30.7
Found (%)	12.3	1.2	7.1	31.2

Table 5-9 Infrared spectrum of the solid product from the reaction of MoF_6 and W in MeCN.

Frequencies $\nu_{max}(cm^{-1})$	Assignment[98]
3010 w	ν_{13} CH_3 str. E
2944 mw	ν_1 CH_3 str. A_1
2322 ms	ν_2 CN str. A_1
2319 sh	
2297 ms	$\nu_3 + \nu_4$
2255 vw	$\nu_1-\nu_{16}$; $\nu_1-\nu_6$
1410 w	ν_{14} CH_3 def E
1364 s	ν_3 CH_3 def. A_1
1028 sh	ν_{15} CH_3 rock E
1019 ms	
953 mw	ν_4 CC str. A_1
941 mw	
720 ms	$2\nu_{12}+\nu_{19}$; $\nu_3-\nu_7$; $\nu_{14}-\nu_{16}$
703 ms	ν_5 MN str. A_1
650 vs	ν_6 MF′ axial str. A_1
635 sh	ν_7 MF_4 equatorial str. A_1
418 w	ν_{17} CCN def. E
285 s	ν_{18} F′-MF_4 def. E
250 s	ν_{19} MF_4 in-plane def. E

frequencies are comparable with the ν_4 mode for MoF_5.NCMe (953 cm^{-1}) and WF_5.NCMe (942 cm^{-1}) respectively. The modes due to the MF_5.N portion appear at the same position as those of the MoF_5.N portion of MoF_5.NCMe.

5-2-5 Reaction of Molybdenum Metal with WF_6 in Acetonitrile

Tungsten hexafluoride can oxidize molybdenum metal at room temperature in MeCN. Unlike other reactions in this series, a green solid was isolated from the solution. The reaction was expected to produce a mixture of Mo^V and W^V complexes with the mole ratio of $Mo^V:W^V$ = 1:5. The elemental analysis for C, H and N was carried out, however, the result does not agree with the expected mole ratio. Another difference from the other products described above is that the green solid did not react with aqueous HNO_3 over the temperature range 20°C-60°C. Because of this behaviour, the atomic absorption analysis for Mo was not possible. The infrared spectrum of the solid state was recorded at room temperature and the data are listed in Table 5-10. From the spectrum it appears that the product contains species with the symmetry of C_{4v} and the complexes MoF_5.NCMe and WF_5.NCMe may be present. However, the green solid was not simply a mixture of MoF_5.NCMe and WF_5.NCMe with the mole ratio of 1:5. Further study is required for the definitive characterization for this product.

The nature of the above four reactions is summarized in Table 5-11. The qualitative order of rate of the reactions observed appears to be as follows:

$$Mo+5MoF_6 > W+5MoF_6 > Mo+WF_6 > W+5WF_6$$

Table 5-10 Infrared spectrum of the solid product from the reaction of WF_6 and Mo in MeCN.

Frequencies ν_{max} (cm^{-1})	Assignment[98] (?)
3010 w	ν_{13} CH_3 str. E
2944 m	ν_1 CH_3 str. A_1
2322 ms	ν_2 CN str. A_1
2297 ms	$\nu_3 + \nu_4$
1410 mw	ν_{14} CH_3 def. E
1365 mw	ν_3 CH_3 def. A_1
1028 s	ν_{15} CH_3 rock E
953 w	ν_4 CC str. A_1
942 w	
720 s	$2\nu_{12} + \nu_{19}$; $\nu_3 - \nu_7$; $\nu_{14} - \nu_{16}$
703 s	ν_5 MN str. A_1
650 vs	ν_6 MF′ axial str. A_1
635 sh	ν_7 MF_4 equatorial str. A_1
418 w	ν_{17} CCN def E
275 ms	ν_{18} F′-MF_4 def. E
240 s	ν_{19} MF_4 in-plane def. E

Table 5-11 The summary of the nature of the reactions M + MF_6 (M = Mo, W) in MeCN.

	Mo	W
MoF_6	$Mo+5MoF_6+6MeCN \rightarrow 6MoF_5.NCMe$ Yellow product (1)* Fast	$W+5MoF_6+8MeCN \rightarrow WF_5.5MoF_5.8MeCN$ (?) Yellow product (2)* Reasonably slow
WF_6	$Mo+WF_6 \rightarrow$ Green product (3)* Slow	$W+5WF_6+6MeCN \rightarrow 6WF_5.NCMe$ Yellow product (4)* Slow

*(1)~(4) The amount of product decreases as the number increases.

It seems that the important features affecting rate and yield are the properties of the oxidizing agents, and then the nature of the metals Mo and W.

5-2-6 The Interaction between MoF_5.NCMe and Bu_4NI in CH_2Cl_2

The reaction between MoF_5.NCMe and Bu_4NI produces a brown sponge like solid at room temperature. The solid was formed immediately. Although the solvent removed by distillation had no apparent pink colour, the electronic spectrum of this solvent contained a band at 505 nm with very low intensity due to the presence of trace iodine. When the reaction was allowed to proceed for a longer period at room temperature, no other change was observed. Attempts to record an infrared spectrum of the brown solid were unsuccessful, because it did not mull satisfactorily. The brown solid was soluble in MeCN, and the electronic spectrum of the solution had a cut off at about 400 nm.

5-2-7 The Redox Property of MoF_5.NCMe in MeCN.

The cyclic voltammogram of MoF_5.NCMe in MeCN at a platinum electrode showed quasi-reversible waves due to Mo^{VI}/Mo^{V} and Mo^{V}/Mo^{IV} couples with peak to peak separations of 0.093V and 0.22V respectively. The half-wave potentials obtained from the voltammogram were $E_{\frac{1}{2}}(Mo^{VI}/Mo^{V})$ = 1.63V and $E_{\frac{1}{2}}(Mo^{V}/Mo^{IV})$ = -0.075V vs. Ag^{+}/Ag. The assignment of these couples were made by comparison with the study of hexafluoromolybdate(V) salts in MeCN (Chapter Four). The half-wave potential due to Mo^{V}/Mo^{IV} couple in MoF_5.NCMe occurs at a less negative value than in MoF_6^- which suggests that MoF_5.NCMe should

be capable of oxidizing I^- to release I_2 (Table 5-12). However, if such a reaction does occur it is very slow (Section 5-2-6). The half-wave potential value of the Mo^{VI}/Mo^{V} couple in MoF_5.NCMe is very similar to that observed from MoF_6^- salts.

5-2-8 The Reaction between CuF_2 and MoF_5.NCMe in MeCN.

The fluoride, CuF_2 is insoluble in MeCN. The reaction between CuF_2 and MoF_5.NCMe was extremely slow. After the reaction mixture was shaken overnight, a small amount of pale green solid was isolated from the solution. There was still unreacted CuF_2 left in the solution, even though equi—equivalents of CuF_2 and MoF_5.NCMe were used. The resulting pale green solid is sensitive to moisture. The electronic spectrum of the pale green solid contained an absorption band at 720 nm due to Cu^{2+}. The infrared spectrum of the solid contains two strong bands at 635 cm^{-1} and 250 cm^{-1}, which can be assigned to the ν_3 and ν_4 vibrations of the hexafluoromolybdate(V) ion respectively (Table 5-13). According to these observations, the reaction appears to be as follows (equation 5-5).

$$CuF_2 + 2MoF_5.NCMe \xrightarrow{MeCN} Cu^{2+}(solv.) + 2MoF_6^- \qquad (5\text{-}5)$$

This is a Lewis acid-base reaction. Although acetonitrile has a good solvating property, the complex MoF_5.NCMe is not a very good fluoride ion acceptor, since the reaction was very slow and incomplete.

Table 5-12 Comparison of half-wave potentials $E_{\frac{1}{2}}V$ vs. $Ag^{+}(0.1\ mol\ dm^{-3})/Ag^{\circ}$ of $MoF_5.NCMe$ and Bu_4NI in MeCN

Solid species ($10^{-2}\sim10^{-3}$ mol dm^{-3})	Mo^{VI}/Mo^{V}	I_2/I_3^-	Mo^{V}/Mo^{IV}	I_3^-/I^-
$MoF_5.NCMe$	1.63 (0.093)		-0.075 (0.22)	
Bu_4NI		0.30 (0.11)		-0.19 (0.34)

Table 5-13 Infrared spectrum of the product from the reaction

$$CuF_2 + 2MoF_5.NCMe \xrightarrow{MeCN} Cu^{2+}(solv.) + 2MoF_6^-.$$

Frequencies $\nu_{max}(cm^{-1})$	Assignment
2325 s	C≡N str.
2299 m	comb.
1020 m	CH_3 rock.
953 mw	CC str.
720 w	
635 vs	$\nu_3(MoF_6^-)$
405 w	CCN def.
250 s	$\nu_4(MoF_6^-)$

5-3 CONCLUSION

Pentavalent solvated molybdenum and tungsten pentafluoride complexes can be prepared by the reduction of hexafluorides using their respective metal powders at room temperature.

Acetonitrile is a good ligand for the stabilization of tungsten(V) with respect to disproportionation.

The vibrational spectra of these complexes are very characteristic, and very similar to that of SbF_5.NCMe.

5-4 EXPERIMENTAL

5-4-1 Preparation of MoF_5.NCMe

(a) The preparation - 1

This preparation was made by reacting the parent materials MoF_5 and MeCN in all glass apparatus. The pentafluoride (about 5 mmol) contained in a breakseal vessel was joined to the vacuum line, meanwhile another fresh break seal vessel was joined to the line next to the previous one. The glass apparatus was flamed out using a gas-oxygen torch. Purified MeCN was attached to the line beside these two breakseal vessels. The apparatus in use was isolated from the vacuum pumps by closing one of the stopcocks. The breakseal vessel containing MoF_5 was opened by breaking the seal using a glass sheathed iron bar and a magnet. The pentafluoride was transferred from the original vessel to the fresh empty one by vacuum distillation using liquid N_2. When the distillation was progressing, it was necessary to heat the original breakseal vessel containing pentafluoride using a hair dryer. When all

the pentafluoride was transferred to the fresh breakseal vessel, the solvent MeCN (10 cm^3) was added to MoF_5. The breakseal vessel containing the mixture was sealed from the vacuum line, allowed to warm to room temperature and shaken for a moment. The vessel was joined to the vacuum line again. The breakseal was broken by a glass sheathed iron bar, then the excess solvent was removed by vacuum distillation and a pale yellow solid was obtained. The vessel was sealed again with the sample. The infrared spectrum of the solid was recorded and the data are shown in Table 5-1.

(b) The preparation - 2

Molybdenum metal powder was dried by pumping on the vacuum line at 150°C before use. A one limb vessel equipped with a Rotaflo or a J. Young stopcock was loaded with molybdenum powder in the laboratory and slowly evacuated on the vacuum line. It was heated with oil bath at about 150°C for six hours under dynamic vacuum conditions. The vessel was closed and taken into the glove box. The metal powder was transferred to the original brown bottle and stored in glove box for use.

An evacuated and flamed out double limb vessel was loaded with the molybdenum powder (1 mmol) in the glove box, then the vessel was re-evacuated on the vacuum line. Acetonitrile (10 cm^3) and MoF_6 (5 mmol) were added by vacuum distillation at -196°. On warming to room temperature a very pale yellow solution was obtained over the Mo powder. The solution was shaken by hand for about two minutes, and the pale yellow colour of the solution became deeper. The vessel was attached to the vacuum line, and the solution was decanted into the empty limb of the vessel after the

unreacted metal powder had settled down completely. The volatile materials were removed by vacuum distillation, and a pale yellow solid was obtained. This solid was sealed in this limb and used for further analysis. The quantitative analysis for molybdenum was made using atomic absorption spectroscopy, and carbon, hydrogen and nitrogen were analyzed by microanalyses in the Department. The analysis for fluorine was carried out in West Germany (Analytische Laboratorien). The infrared spectra of the product are listed in Table 5-4 for the H isotopic complex and in Table 5-5 for the D isotopic complex.

5-4-2 Preparation of WF_5.NCMe

The tungsten metal powder was dried using the method used for drying molybdenum powder described in section 5-4-1.

The preparation of WF_5.NCMe was very similar to the preparation -2 for MoF_5.NCMe. Tungsten powder (1 mmol) was placed into an evacuated and flamed out double limb vessel in the glove box. Acetonitrile (10 cm^3) and WF_6 (5 mmol) were distilled into the vessel. When the mixture was allowed to warm to room temperature, a colourless solution over the metal powder was obtained. After the mixture was shaken for two hours, no colour change was observed. The mixture was left shaking overnight, and a pale yellow solution was obtained. After the unreacted tungsten powder had completely settled down, the volatile materials were removed and a pale yellow solid product was isolated. The quantity of the yield was much smaller than that of MoF_5.NCMe of

preparation -2. The carbon, hydrogen and nitrogen were analyzed using microanalysis. The fluorine analysis was also carried out in West Germany (Analytische Laboratorien). The infrared spectrum was recorded and the frequencies are listed in Table 5-4.

5-4-3 Reaction of Tungsten Metal with MoF_6 in MeCN.

The loading of chemicals was the same as that of the preparation of WF_5.NCMe. When the mixture was allowed to warm to room temperature, a very pale yellow colour was observed. The mixture was shaken for six hours and a pale yellow solution was obtained. After the removal of the volatile materials, a pale yellow solid was isolated. The molybdenum content was analysed by atomic absorption spectroscopy and C, H and N were analysed by microanalyses. The infrared spectroscopic data are listed in Table 5-9.

5-4-4 Reaction of Molybdenum Metal with WF_6 in MeCN.

The chemicals were mixed following the procedure described in section 5-4-2. When the mixture was allowed to warm to room temperature, the solution was colourless. After it was shaken for two hours, a very pale green solution was observed. The mixture was left shaking overnight, and a pale green solid was isolated from the resulting solution. The data for the infrared spectrum are shown in Table 5-10.

5-4-5 Reaction of MoF_5.NCMe with Bu_4NI in CH_2Cl_2.

The iodide, Bu_4NI (0.5 mmol) was loaded into a frangible ampoule and sealed as described in section 3-4-5. The ampoule and MoF_5.NCMe (0.5 mmol) were placed into a flamed out double limb vessel in the glove box. Dichloromethane (10 cm^3) was added. After MoF_5.NCMe was dissolved, the frangible ampoule was broken. When the reactants were mixed, the solution became brown immediately and a brown sponge like solid was isolated from the resulting solution. An electronic spectrum showed there were traces of iodine in the removed solvent.

5-4-6 Reaction of CuF_2 and MoF_5.NCMe in MeCN.

Previously dried difluoride CuF_2, (0.2 mmol) and MoF_5.NCMe (0.4 mmol) were loaded into a flamed out double limb vessel in the glove box. Acetonitrile (10 cm^3) was distilled into the vessel and the MoF_5.NCMe was dissolved. The difluoride CuF_2 was not soluble in MeCN. After the mixture was shaken for two hours, there was no sign of change. The mixture was left shaking overnight, and a pale green solid was isolated from the resulting solution. The infrared spectrum contained bands which are listed in Table 5-13. The electronic spectrum had a band at λ_{max} 720 nm due to the presence of the Cu^{2+} ion.

CHAPTER SIX

CONCLUSIONS

Individual conclusions from the results of previous chapters have already been described in the respective chapters. In this chapter, a brief overview of the conclusions will be presented.

High oxidation state transition metal fluorides such as MoF_6 and WF_6 are easily reduced by the ionic iodide, Bu_4NI, to MoF_6^- and WF_6^-, releasing I_2, in the solvents CH_2Cl_2 and SO_2. Although this is true for NaI and KI in SO_2, which is in agreement with previous work,[41] the reduction of MoF_6 and WF_6 by NaI and KI in CH_2Cl_2 is extremely slow and incomplete. This appears to be due to the insolubility of these iodides in this solvent. Other workers have shown that the analogous reaction involving MoF_6 in MeCN leads to further oxidation of I_2 to give $[I(NCMe)_2][MoF_6]$. The products are I_2 and a mixture of WF_6^- and WF_7^- salts if the oxidizer is WF_6 in MeCN.[8]

Although MoF_6^- is reduced to MoF_6^{2-} in SO_2 by alkali metal iodides, for example NaI, this is not observed with Bu_4NI in CH_2Cl_2 and SO_2. The cyclic voltammetry studies of these compounds show that MoF_6^- cannot be reduced by the iodides in MeCN and CH_2Cl_2 under the conditions where the concentrations of MoF_6^- and iodides are similar. It is not surprising that the iodides cannot reduce the even weaker oxidizer WF_6^- to W^{IV}.

In these reactions, the solubilities of iodides are important for successful syntheses. In dichloromethane, Bu_4NI is superior to the inorganic iodides such as NaI and KI whereas all the reactions are quite straightforward in SO_2. The different

nature of MoF_6 and WF_6 is reflected in the observed reaction rates. All the reactions involving MoF_6 appear to be faster compared with those involving WF_6.

Molybdenum hexafluoride is reduced to $(MoF_5)_4$ by molybdenum metal powder slowly at about 150°C under heterogeneous conditions in agreement with previous work. However, MoF_6 is readily reduced to the pentavalent complex MoF_5.NCMe by molybdenum powder in MeCN at room temperature. Furthermore, MoF_6 can be reduced also by tungsten metal powder in MeCN at room temperature. The product appears to be a mixture of solvated pentavalent MF_5 complexes of molybdenum and tungsten. Similarly, tungsten hexafluoride is reduced by tungsten powder under the conditions described above to give the pentavalent complex WF_5.NCMe. Although the pentafluoride, $(WF_5)_4$ is unstable with respect to disproportionation to WF_4 and WF_6, the complex WF_5.NCMe is stable at room temperature. Tungsten hexafluoride can be reduced by molybdenum metal powder, although the nature of the product is not clear.

The complex MoF_5.NCMe interacts with Bu_4NI in CH_2Cl_2 to produce a trace of I_2. The cyclic voltammetric study of MoF_5.NCMe in MeCN indicates that the half-wave potential of the couple Mo^V/Mo^{IV} is slightly less negative than that of the couple I_3^-/I^- for Bu_4NI. From this, it is suggested that there is a possibility of MoF_5NCMe oxidizing Bu_4NI in MeCN. The reaction of MoF_5NCMe with CuF_2 in MeCN is very slow, suggesting that MoF_5.NCMe is not a strong fluoride ion acceptor.

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